Synthesis of New Ruthenium Complexes for Propargylic Substitution Reactions

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A Thesis Presented to

the Faculty of the Department of Chemistry

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

Dong Hyun Koo

August 2013

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Dong Hyun Koo

APPROVED:

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Dr. Jeremy A, May

_____

Dr. Allan J. Jacobson

_____

Dr. Olafs Daugulis

_____

Dr. T. Randall Lee

_____

Dr. Lars C. Grabow

_____

Dean, College of Natural Sciences and Mathematics

Dedicated to my parents

Uiseo Koo and Limsoon Song

for their encouragement and support

in all of my life's endeavor

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ABSTRACT

This thesis is concerned with the synthesis of monomeric ruthenium complexes and diruthenium complexes with Tp or Cp derivatives and their ruthenium-catalyzed propargylic substitution reactions. First, the mononuclear ruthenium complex, ^{Cl}TpRu(COD)Cl was synthesized by the simple method of treating TpRu(COD)Cl with sulfonyl chloride. The catalytic activity for propargylic substitution reactions with aromatic propargylic alcohols was good, but the substrate scope was limited to those substrates. Second, reactions of [Cp^RuCl(μ-Cl)$_2$RuCp^Cl] (Cp^ : 1,4-di-tert-butyl-2-neopentyl-3-methoxy-cyclopenta-1,3-diene) with $MeSSiMe_3$ in CH_2Cl_2 at room temperature afforded two types of thiolate-bridged dinuclear Ru(III) complexes [Cp^Ru(u-SMe)$_3$RuCp^]Cl or [Cp^RuCl(μ-SMe)$_2$RuCp^Cl] depending upon the number of equivalents of $MeSSiMe_3$. Reaction of Cp^RuCl(μ-Cl)RuCp^Cl] with excess $MeSSiMe_3$ in CH_2Cl_2 resulted in the formation of the triply bridged complex, [Cp^Ru(μ-SMe)$_3$RuCp^]Cl, and 3 equivalent $MeSSiMe_3$ afforded the doubly bridged diruthenium complex, [Cp^RuCl(μ-SMe)$_2$RuCp^Cl]. X-ray crystallography was used to determine their detailed structures, and their catalytic properties were explored in the propargylation of nucleophiles.

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ABBREVIATIONS AND ACRONYMS

COD	1.5-cyclooctadiene
Cp	cyclopentadiene
Cp^	1,4-di-tert-butyl-2-methoxy-5-neopentylcyclopenta-1,3-diene
DCE	dichloromethane
DMF	N,N-dimethyl formamide
DMSO	*N*,*N*-dimethyl sulfoxide
DPPF	1,1'-bis(diphenylphosphino)ferrocene)
Et	diethyl ether
Et_2O	ether
EtOH	ethanol
Hex	*n*-hexane
H_2O	water
KTp	potassium trispyrazolylborate
Me	methyl

MeOH	methanol
Nu	nucleophile
NMR	nuclear magnetic resonance
Ph	phenyl
*t*Bu	*tert*-butyl
THF	tetrahydrofuran
TMEDA	tetramethylethyldiamine
Tp	trispyrazolylborate
XRD	X-ray diffraction

Chapter One

Ruthenium-catalyzed Propargylic Substitution Reactions

1.1 Introduction

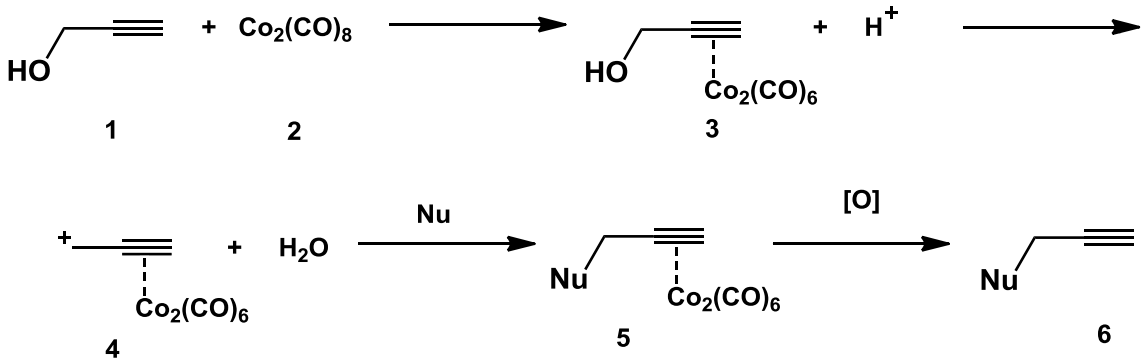
Allylic substitution reactions of allylic alcohol derivatives with nucleophiles catalyzed by transition-metal complexes are very successful and reliable methods in organic synthesis.[1] However, much less attention has been paid to the propargylic substitution reactions of propargylic alcohol derivatives with nucleophiles. One class of propagylic substitution reactions involve the intermediacy of allenylidene ruthenium complexes.[2] These allenylidene ruthenium complexes from propargylic alchols were first described by Selegue in 1982 and used to propargylic substitution reactions with propargylic alcohols.[3] However, the system was limited to aromatic and less hindered propargylic alcohols.[4] To overcome these drawbacks, we designed new ruthenium complexes to expand the substrate scope for propargylic substitution reactions such as aliphatic and hindered propargylic alcohols. This chapter will summarize the previous work that has been performed in this area to date.

1.2 Nicholas Reaction

The Nicholas reaction has been known traditionally to be an effective tool for propargylic substitution reactions.[5] In addition to heteroatom-centered nucleophiles, such

as alcohols, amines, and thiols, a wide variety of carbon-centered nucleophiles, including simple ketones such as acetone, are also useful for the Nicholas reaction. The addition of dicobalt octacarbonyl (**2**) to a prop-2-yn-1-ol (**1**) formed a metal coordinated alkyne **3** (Scheme 1.2.1). Dehydration of **3** gave carbocation (**4**), which is stabilized by the cobalt complex, then the addition of a nucleophile followed by demetallation afforded a new propargylic compound **6**. This reaction, however, has some drawbacks[6]; a stoichiometric amount of $[Co_2(CO)_8]$ is required, and several steps are necessary to obtain propargylic-substituted products from propargylic alcohols via cationic propargyl complexes $[Co_2(CO)_6(propargyl)]^+$.

Scheme 1.2.1: Nicholas Reaction

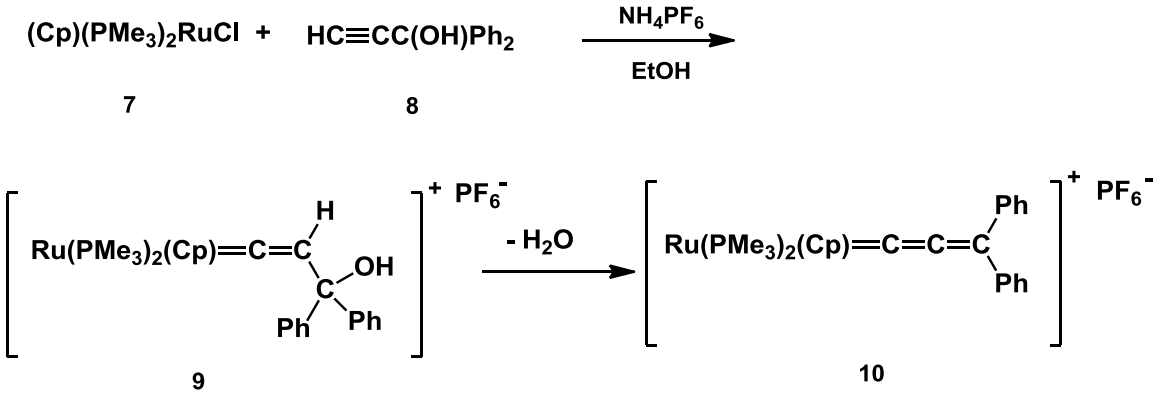


1.3 Ruthenium-Allenylidene Complexes

Allenylidene-metal complexes were first found attractive for the building of carbon-rich structures[7] and in the materials science[8] because they have several

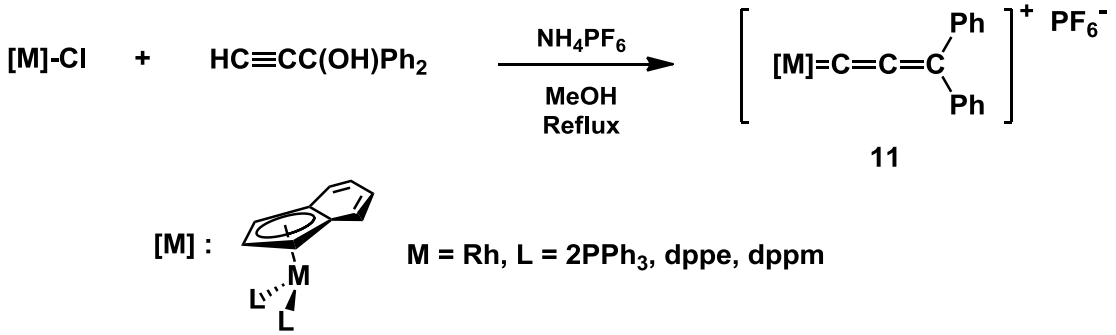
advantages such as their one-dimensional nature, and their use as bridges for electronic communication between a metal site and a remote functionality.[9] Since their first discovery, the chemistry of metal-allenylidenes has been developed into a somewhat general method for activation of propargylic alcohols. Metal-allenylidenes are currently leading to useful applications in the field of homogeneous catalysis[10] for C-C bond formation,[11] alkene metathesis,[12] and selective propargylation.[13] Notably, the propargylation has been most successful using ruthenium complexes via ruthenium-allenylidenes. The most useful method to form metal-allenylidenes was described by Selegue in 1982 for the preparation of $[Ru(=C=C=CPh_2)(\eta^5C_5H_5)PMe_3]_2][PF_6]$ (**10**). This method is based on the spontaneous dehydration of a propargylic alcohol, via the hydroxyl vinylidene intermediate **9** after η^2-coordination of the 2-propyn-1-ol to a 16-electron metal center (Scheme 1.3.1).

Scheme 1.3.1*:* Formation of an Allenylidene Ruthenium Complex by Selegue.

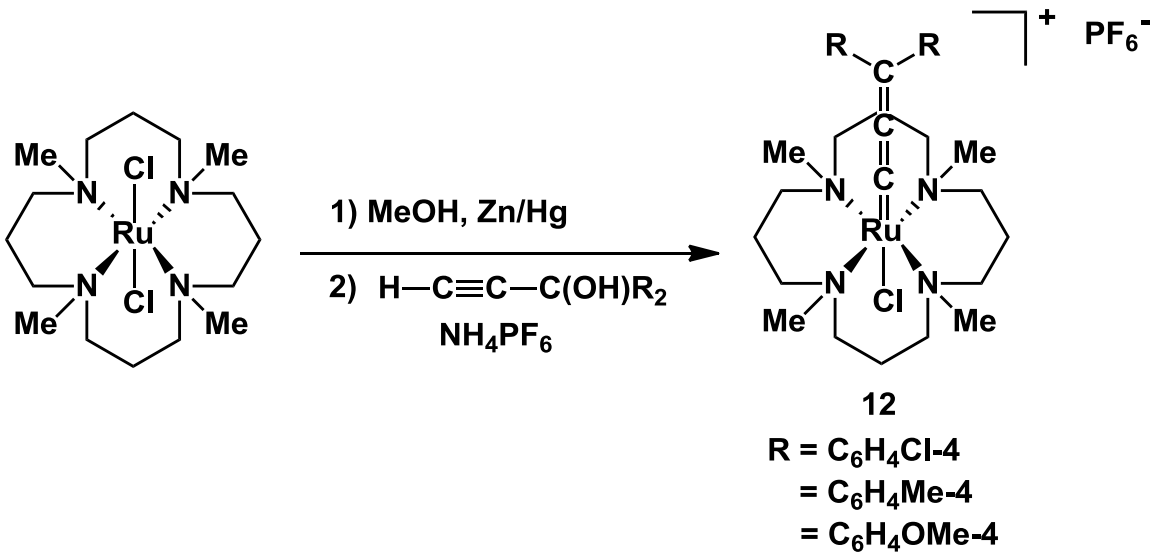


Ruthenium-allenylidene complexes constitute the most extensive allenylidene family.[14] A few groups have used Selegue's method to obtain ruthenium-allenylidenes with various ligand, and substituents, such as the η^5-indenyl ruthenium complexes **11** (Scheme 1.3.2)[15] or tetradentate macrocyclic tertiary amine ligand **12** (Scheme 1.3.3).[16]

Scheme 1.3.2*:* Indenyl Ruthenium Allenylidene Complex



Scheme 1.3.3: Allenylidene Ruthenium Complex with Tetradentate Tertiary Amine Ligand

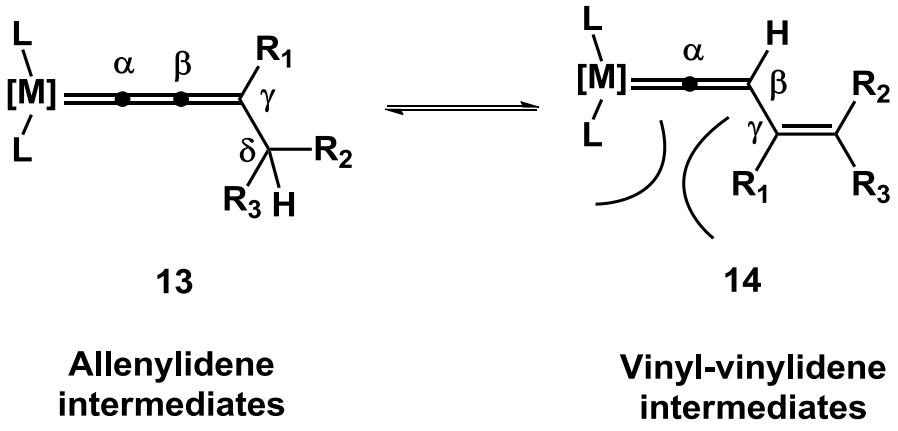


12

R = C_6H_4Cl-4
= C_6H_4Me-4
= C_6H_4OMe-4

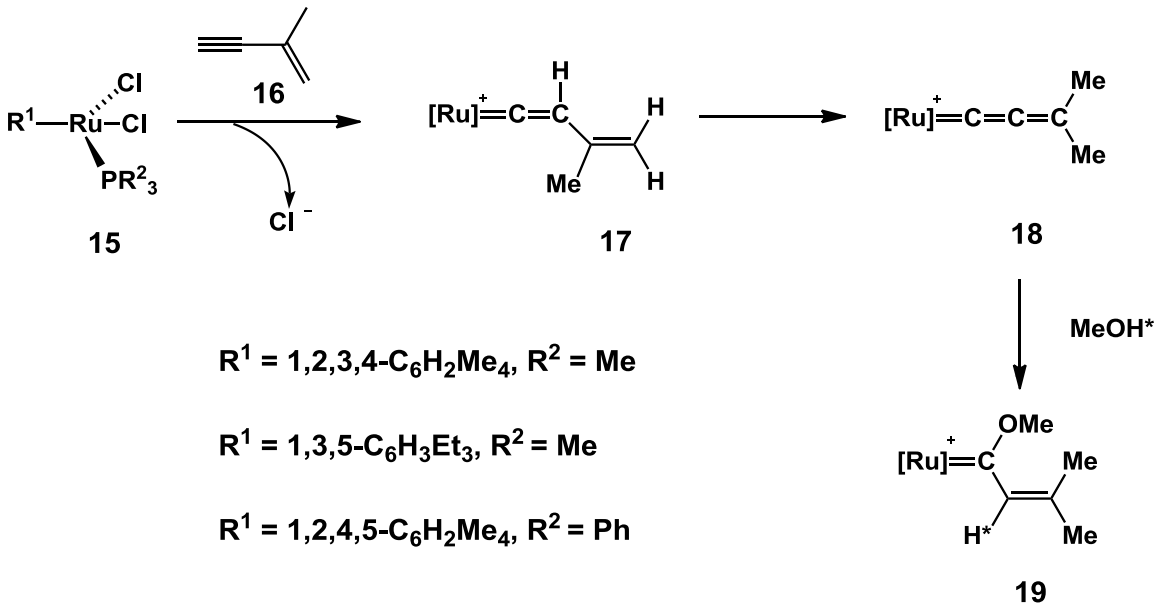
Ruthenium-allenylidene reactivity is highly dependent on the electron-richness of the metal moiety: electrophilic ruthenium complexes lead to highly reactive allenylidenes with electrophilic Cα and Cγ centers while the C_β atom is a nucleophilic site.[17] An increase of the bulkiness or electron-releasing effects of the ligand allow stabilization of allenylidenes for a variety of ruthenium fragments, and their reactivity is focused on the γ carbon atom (Scheme 1.3.4).[18] If a substituent on the γ–carbon is larger, the steric repulsion between ligands on the ruthenium metal and the substituent on the γ–carbon would be bigger. As a result, the vinyl-vinylidene intermediate **14** would become less stable relative to **13**. Thus, electron-richness and steric hindrance could be important factors to form stable allenylidene ruthenium complexes.

Scheme 1.3.4: Steric Factors to Form Stable Allenylidene Ruthenium Complexes.



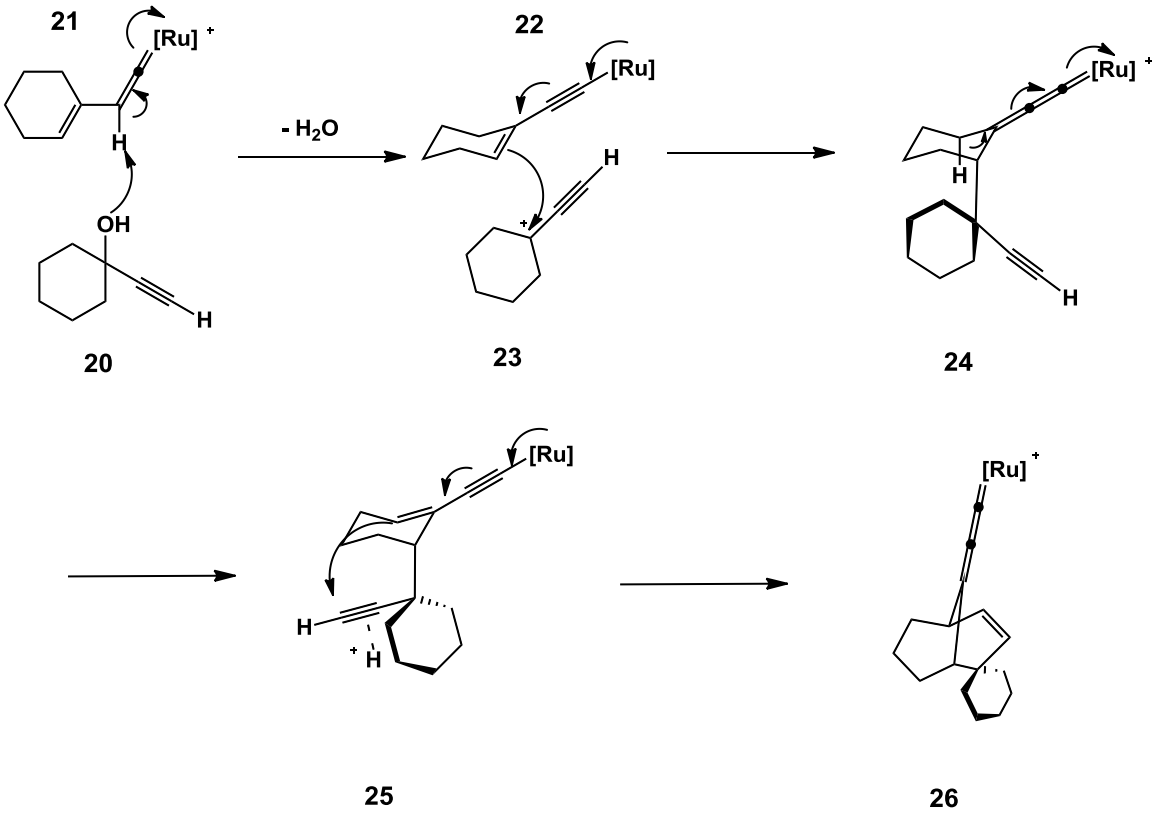
The allenylidene and vinyl-vinylidene ruthenium complex are isomerized in the propargylation. In 1990, Dixneuf observed the formation of an allenylidene ruthenium intermediate **18** by ruthenium precursor **15** and vinylacetylene derivative **16** (Scheme 1.3.5).[19] On the basis of proton-labeling experiments, an allenylidene ruthenium intermediate **18** was formed and reacted with methanol to give complex **19**. The formation of allenylidene ruthenium complex $[Ru=C=C=C(Me)_2]^+$ **18** could be explained by isomerization of the vinyl-vinylidene ruthenium complex, $[Ru=C=C(H)C(Me)=CH_2]+$ **17**. As expected, methanol could attack the α-carbon to form complex **19** since the α-carbon on allenylidene ruthenium complex **18** is electrophilic.

Scheme 1.3.5*:* Isomerization of Allenylidene and Vinyl-vinylidene Formation.



The mechanism for the formation of allenylidene ruthenium complex from the vinyl-vinylidene ruthenium complex was proposed by the Gimeno group in 1999.[20] The first step was the transfer of the acidic vinylidene proton **21** to the propargylic alcohol **20** which generated complex **22** and carbocation species **23**. A carbon-carbon coupling reaction between intermediates took place to form the allenylidene derivative **24**. The deprotonation afforded **25** and the following intramolecular C-C coupling process between the alkenyl and terminal alkyne gives the allenylidene ruthenium complex **26** (Scheme 1.3.6).

***Scheme 1.3.6**:* Proposed Mechanism for the Formation of **26**.

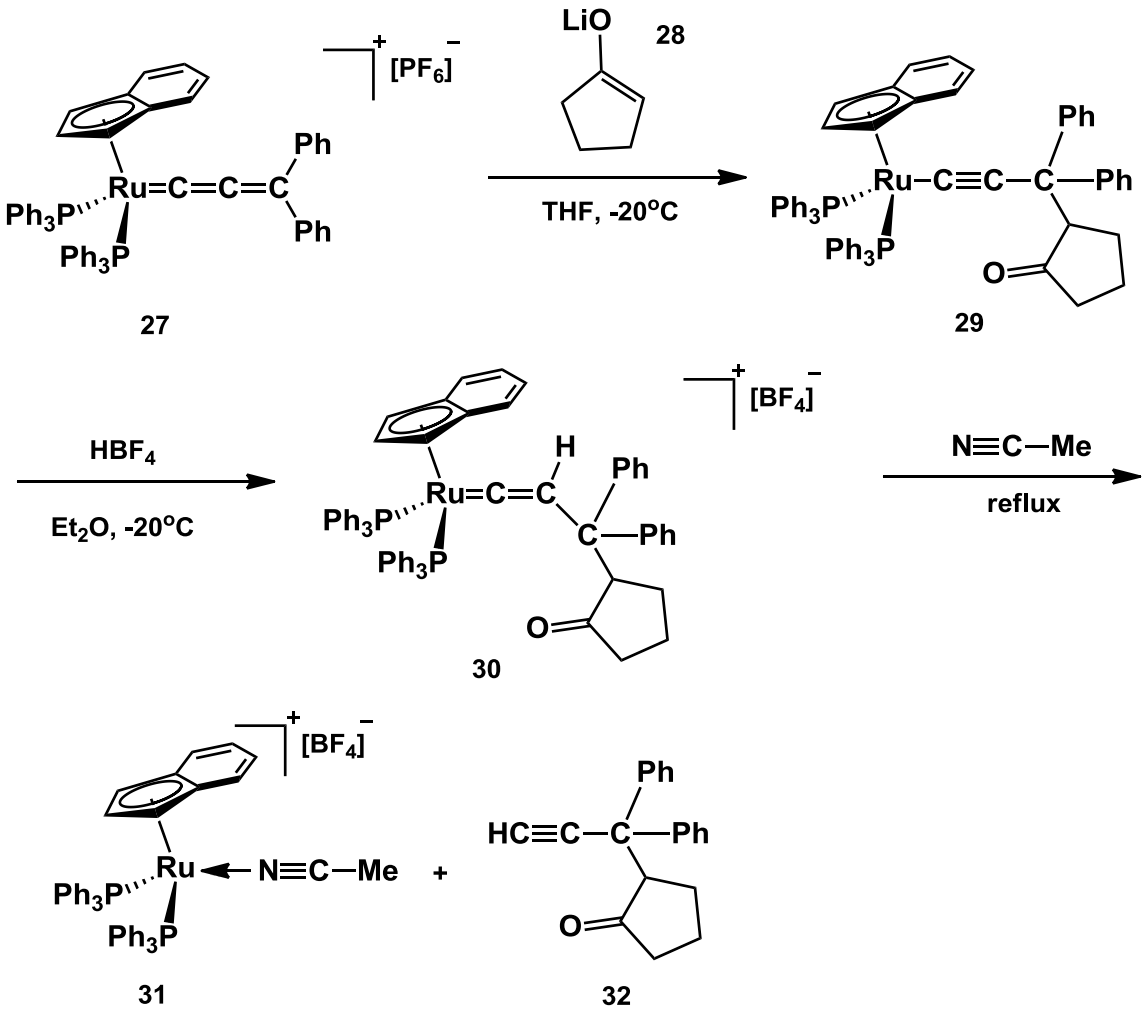


1.4 Mononuclear Ruthenium Complexes and Propargylic Nucleophilic Addition

A few examples were shown that catalytic propargylic nucleophilic substitution reactions were performed by mononuclear ruthenium complexes via allenylidene ruthenium intermediates.[21] The Gimeno group developed the propargylic nucleophilic addition reactions with $[Ru{=}C{=}C{=}CPh_2(\eta_5\text{-}C_9H_7)(PPh_3)_2]^+$ **27**.[22] This allenylidene ruthenium complex reacted with the lithium enolate of cyclopentanone **28** to give

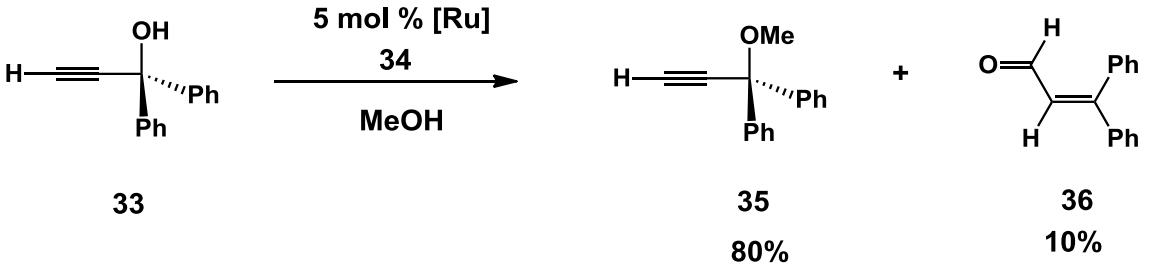
complex **29** (Scheme 1.4.1). The addition of HBF_4 to **29** formed vinylidene complex **30**. Finally, refluxing with acetonitrile afforded complex $[Ru(NCMe)(\eta_5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ **31** and a γ-keto acetylene **32**.

Scheme 1.4.1*:* Mononuclear Ruthenium Catalysts for Propargylic Nucleophilic Addition.



The Gimeno group also developed a propargylic nucleophilic substitution reaction with propargylic alcohols in the presence of [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6)] (Scheme 1.4.2).[23] The reaction of 1,1-diphenyl-2-propyn-1-ol **33** with **34** in methanol gave propargylic ether derivative **35** as a major product, and 3,3-diphenylacrylaldehyde **36**.

Scheme 1.4.2: Mononuclear Ruthenium–catalyzed Propargylation of Propargylic Alcohol.

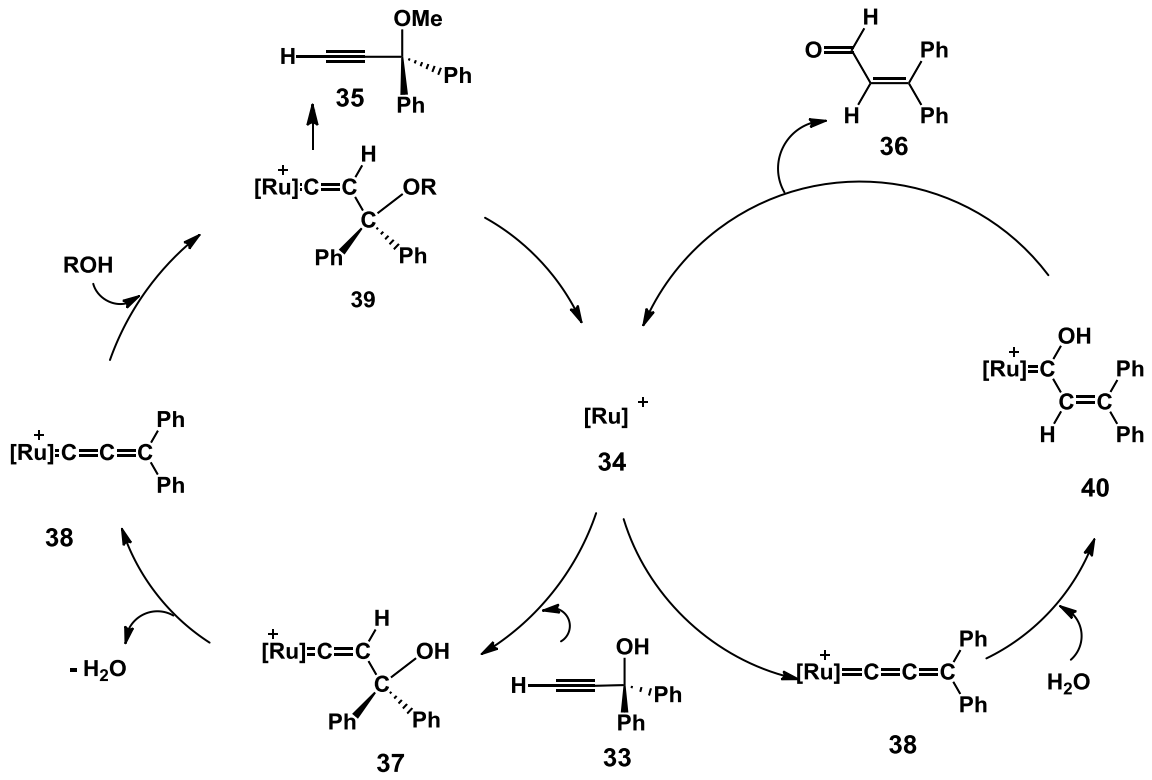


[Ru] = [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6]
(dppf = 1,1`-bis(diphenylphosphino)ferrocene)

The possible mechanism of the formation of compound **35** was suggested in Scheme 1.4.3. First, the allenylidene ruthenium complex **38** could be formed from complex **34** and propargylic alcohol **33** via vinylidene ruthenium intermediate **37**. Then, the nucleophilic addition of methanol to the γ-carbon in allenylidene ruthenium complex would finally afford the product **35**. On the other hand, the readdition of water to **38**

could give the intermediate **40** in which reductive elimination would occur to give the isomerization product **36**.

Scheme 1. 4. 3*:* Proposed Mechanism of Propargyliation with Propargylic Alcohol.



[Ru] = [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (dppf = 1,1`-bis(diphenylphosphino)ferrocene)

It was found that the mononuclear ruthenium complexes could be used for propargylic substitution reactions; however, they did not turn over and both the α- and γ-carbon in the allenylidene ruthenium intermediates were reactive. To overcome those

drawbacks, diruthenium complexes were studied as efficient catalysts for propargylic substitution reactions.

1.5 Dinuclear Ruthenium Complexes and Propargylic Nucleophilic Addition Reactions

In the last decade, Hidai, Nishibayashi, Uemura, and co-workers developed a diruthenium-catalyzed process in which a wide variety of nucloephiles can be used (Figure 1.5.1). Oxygen-, nitrogen-, and phosphorus-centered nucleophiles such as alcohols, amines, amides, and phosphine oxide are available for catalytic propargylic substitution reactions with catalyst **41**.[24]

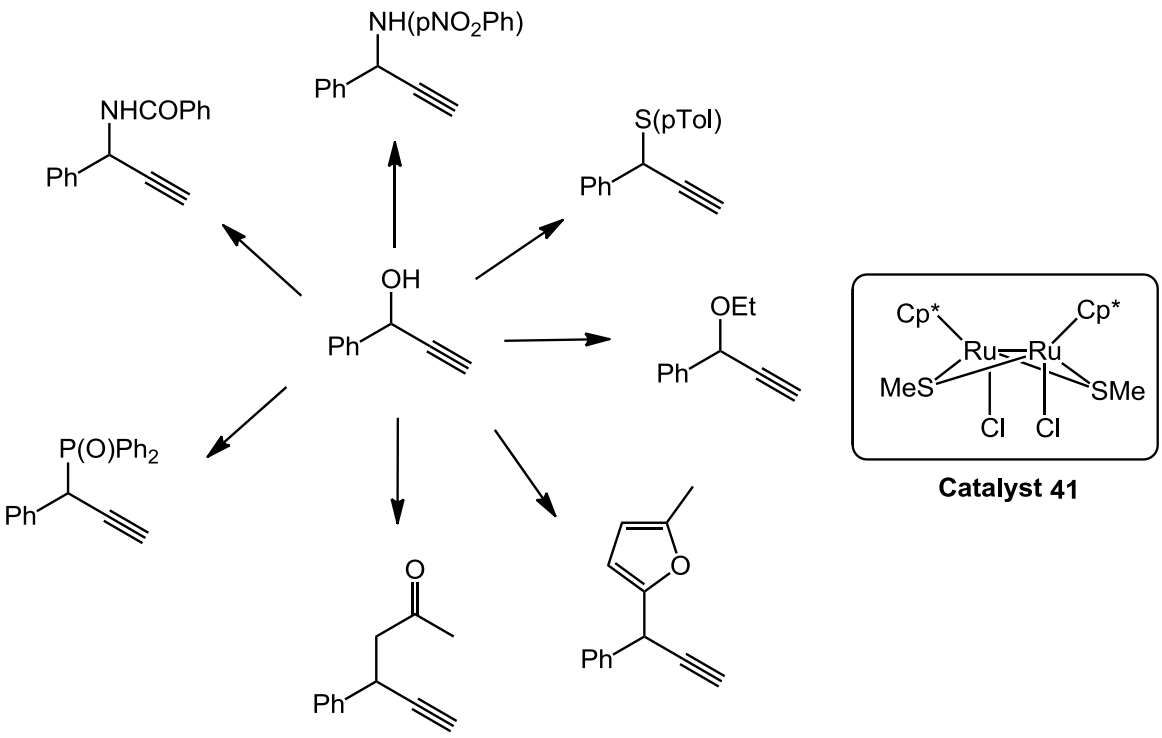
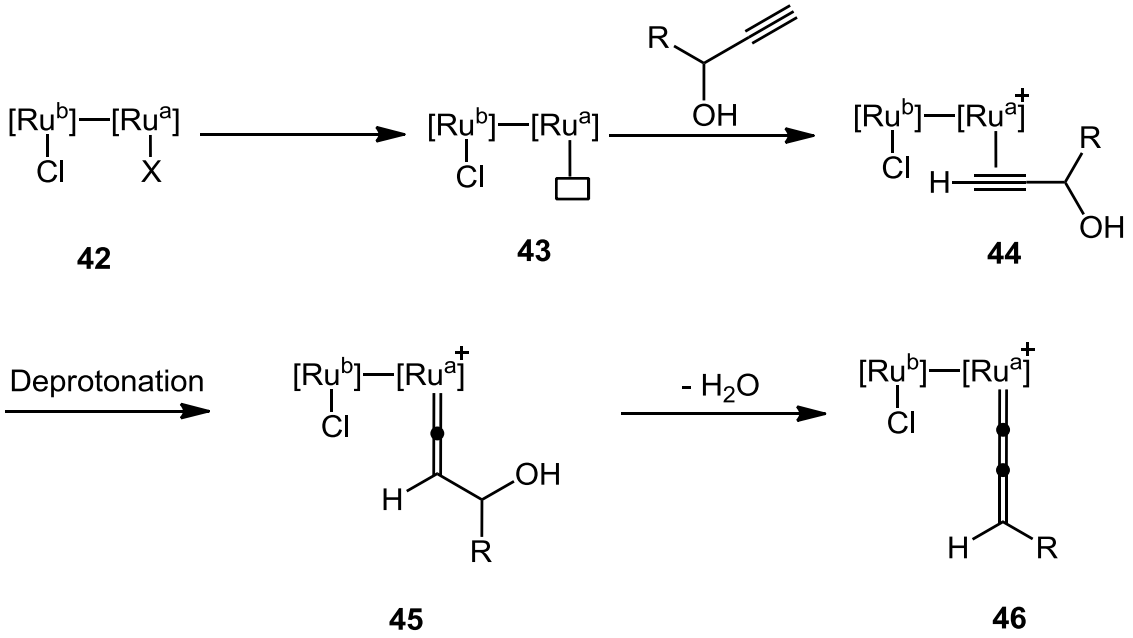


Figure 1.5.1. Thiolate-bridged Diruthenium Catalyzed Propargylic Substitution.

Dinuclear ruthenium complexes compared to mononuclear ruthenium complexes have some benefits for propargylic substitution reactions. The Ru^b in **42** acts as a ligand with the same electron configuration as Ru^a (Scheme 1.5.1). It stabilizes on an open Ru^a coordination site during substrate turn over. In the reaction with MeOH as solvent, dinuclear ruthenium compounds afford a lower energy reaction pathway through intermediate **45** than mononuclear ruthenium compounds during the formation of allenylidene ruthenium intermediate complexes **46**. Furthermore, while deprotonation on the carbon in complex **44** occurred, the bond between the ruthenium atom and carbon in complex **45** became longer. Contrarily, when the dehydroxylation from ruthenium complex **45** occurred to give an allenylidene ruthenium complex **46**, the bond between

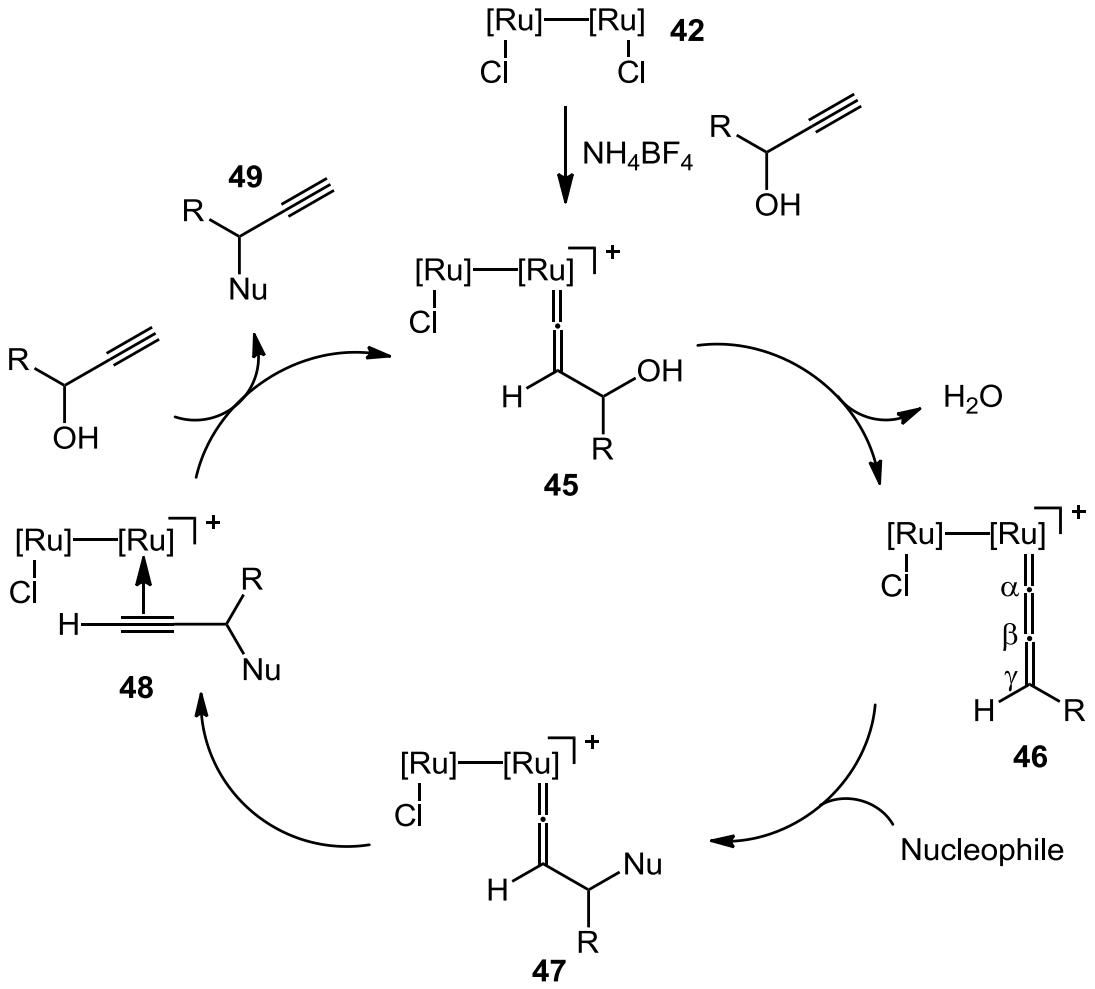
ruthenium atom and carbon became shorter. This change indicates decreasing and increasing back-donation, respectively. In other words, a stable allenylidene ruthenium complex could be formed. Additionally, during deprotonation and dehydroxylation, dinuclear ruthenium complexes had a lower activation free energy than mononuclear ruthenium complexes. The lower activation barriers were due to lower back-donation ability of the dinuclear ruthenium complexes. Finally, dinuclear ruthenium complexes could keep their dimetallic structure during the reactions of their chalcogenolate (S, Se and Te)-bridges. In short, the Ru^a atom in ruthenium compound **46** acted as the catalytic site for nucleophilic substitution reactions with heteroatom or carbon-centered nucleophiles.

Scheme 1.5.1: Allenylidene Ruthenium Formation from a Dinuclear Ruthenium Complex.



The mechanism of the propargylic substitution reaction with the diruthenium catalysts is described in Scheme 1.5.2.[25] First, a cationic diruthenium complex forms a π-complex with a propargylic alcohol. Then, proton migration took place to form complex **45**. The complex **45** spontaneously dehydrates to give the allenylidene ruthenium complex **46**. The addition of a nucleophile gives a vinylidene complex **47**. Finally, the propargylic product **49** is eliminated and the active diruthenium catalyst is regenerated.

Scheme 1.5.2 The Mechanism of Propargylation with Diruthenium Catalysts.



In summary, thiol-bridged diruthenium complexes could be used sub-stoichiometrically for propagylic substitution reactions with various nucleophiles. Nevertheless, tertiary and aliphatic propargylic alcohols were rarely studied for propargylic substitution reactions. These limitations were our initiative to develop novel ruthenium catalysts for propagylic substitution reactions.

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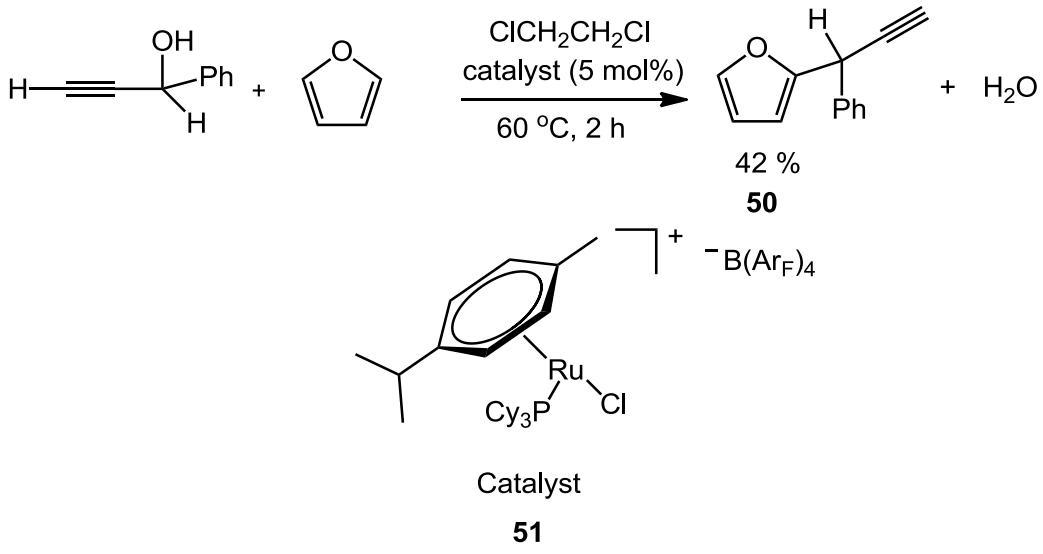
Chapter Two

Synthesis and Catalytic Activity of Monoruthenium Complexes with Tp

2.1 Background and Specific Aims

Several catalytic propargylic substitution reactions have been reported with ruthenium,[13] rhenium[26] and palladium.[27] In particular, Dixneuf has examined catalytic propargylation by mononuclear ruthenium complexes via allenylidene ruthenium intermediates.[21] The Ru complex [(p-cymene)$RuCl_2(PR_3)$ **51** was shown to be a mononuclear catalyst precursor to perform catalytic propargylation (Scheme 2.1.1).

Scheme 2.1.1*:* Propargylic Substitution Reaction with a Mononuclear Ruthenium Catalysts



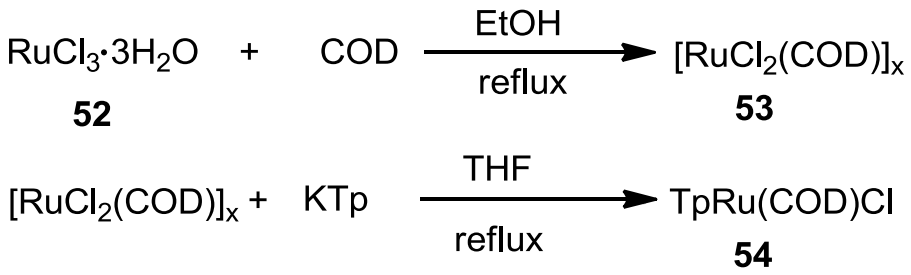
Despite the significant advances made in ruthenium complexes, the catalytic transformation in monoruthenium-mediated propargylic substitution has not been widely investigated. Moreover, the catalytic activity of propargylic substitution reaction such as turnover number was low with mononuclear ruthenium complexes. These considerations led us to envision different ruthenium complexes.

2.2 Results and Discussion.

2.2.1 Synthesis of Monoruthenium Complexes with Tp

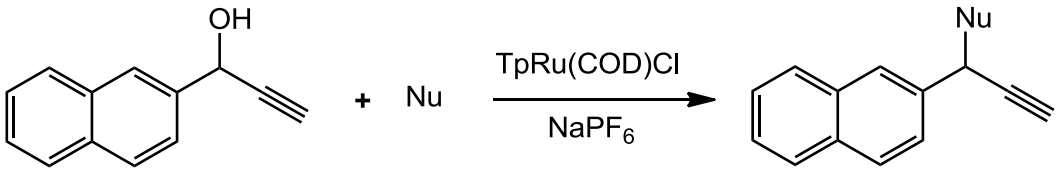
TpRu(COD)Cl was synthesized using the two-step protocol described in Scheme 2.2.1.1. We prepared $Ru(COD)Cl_2$ from $RuCl_3 \cdot 3H_2O$ with a direct ligand substitution by COD. Reduction of the metal precursor by COD and substitution of the resultant ruthenium(II) were carried out in ethanol under reflux conditions. The ruthenium (II) complex **54** was characterized using ^1H NMR and XRD.

Scheme 2.2.1.1 Synthesis of TpRu(COD)Cl, **54**



The propargylation activity with this catalyst was examined in a test reaction of 2-naphthyl propargylic alcohol with different nucleophiles (Table 2.2.1).

Table 2.2.1.1. Catalytic Activity of Various Nucleophiles in Propargylic Substitution Reactions.



55 **56**

Entry	Nucleophile	product
1	acetone	< 5 %
2	ethanol	< 5 %
3[b]	2-methylfuran	18 %

[a] Reaction conditions: 2-naphthylpropanol(0.137 mmol), nucleophiles (2. 74 mmol). TpRu(COD)Cl (20 mol %), $NaPF_6$ (20 mol %)
[b] solvent was 1,2-dichloroethane

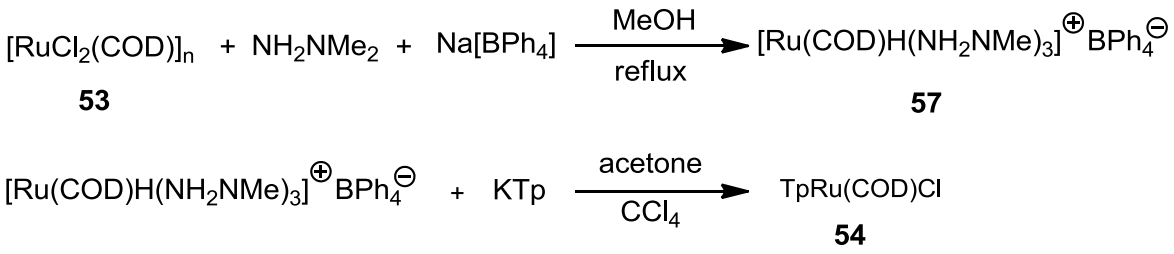
It was found that the nature of the nucleophiles plays a crucial role in the catalytic activity of the ruthenium catalyst. For example, while the yield of the acetone and ethanol products was below 5 % after 12h (entry 1 and 2), the change of the nucleophile to 2-methylfuran resulted in better activity under otherwise identical conditions (entry 3). 1, 2-

dichloroethane was the solvent of choice and other solvents were much less satisfactory in the reaction. On the other hand, no reaction was observed when no ruthenium catalyst was employed in the reaction.

2.2.2 Modified Mononuclear Ruthenium Complexes

The exploration of other ruthenium catalysts was also carried out for the propargylic substitution reaction. While the scale-up for the preparation of TpRu(COD)Cl, the reaction procedure mentioned above (Scheme 2.2.1.1 method) was not reproducible. It only gave the small amount of TpRu(COD)Cl. Then, the alternative method was introduced for large scale reactions (Scheme 2.2.2.1).[28]

Scheme 2.2.2.1 The Alternative Method to Prepare TpRu(COD)Cl



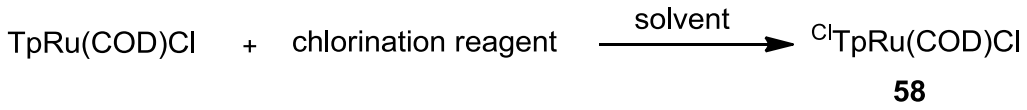
53 **57** **54**

Treatment of a suspension of **53** in methanol with anhydrous dimethyl hydrazine rapidly gave a pale red solution from which the salt **57** was isolated in high yield (96 %) after addition of an aqueous solution of $Na[BPh_4]$. Then, the salt **57** and KTp was heated

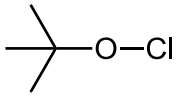
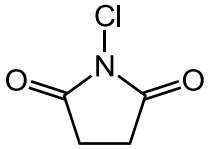
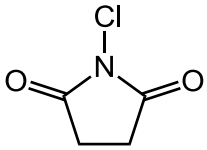
in acetone and CCl_4 to give a dark orange solution from which TpRu(COD)Cl precipitated in a crystalline form.

We next modified the electron density of the trispyrazole ring with an electron withdrawing group, chlorine (Cl). This modification was performed by chlorination with various chlorination reagents starting from TpRu(COD)Cl (Table 2.2.2.1). The use of t-butylhypochlorite as a chlorination reagent showed no activity (entry 1). N-chlorosuccinimide in the presence of benzoyl peroxide or t-butyl hydroperoxide resulted in good yields (entries 2, 3). In addition, the use of sulfonyl chloride brought about higher yields both in the presence of t-butyl hydroperoxide and without additive (entries 4, 5).

Table 2.2.2.1 Chlorination of Tripyrazole Ring in TpRu(COD)Cl



58

Entry	chlorination reagents	additives	solvent	yield
1		–	CCl_4	0 %
2		$(PhCOO)_2$	THF	81 %
3		$(CH_3)_3COOH$	DMF	83 %
4	SO_2Cl_2	–	THF	92 %
5	SO_2Cl_2	$(CH_3)_3COOH$	THF	93 %
6[b]	SO_2Cl_2	–	THF	89 %

[a] Reaction conditions: TpRu(COD)Cl(0.109 mmol), chlorination reagents (0.219 mmol) additives (20 mol %),
[b] large scale reaction; TpRu(COD)Cl (2.48 mmol)

This compound was characterized by ^{1}H-NMR and X-ray crystallography. The structure determined from X-ray crystallography is depicted in Figure 2.2.2.1. One chlorine was substituted at the pyrazole ring in the 2-position and COD is coordinated with ruthenium. One chloride is attached to ruthenium directly. The central ruthenium oxidation state is Ru(II).

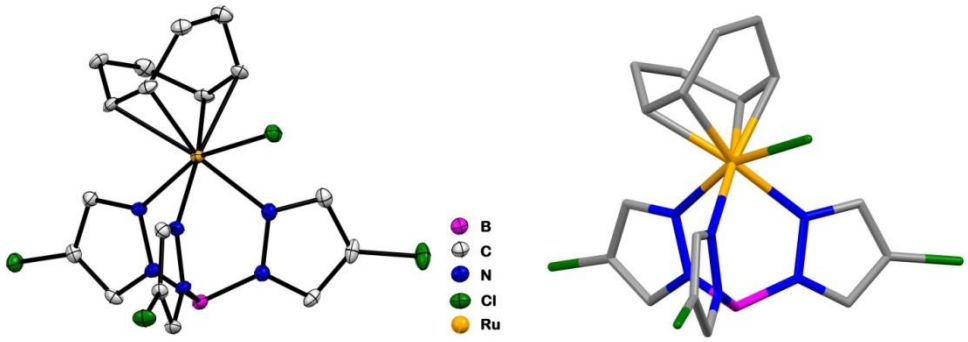
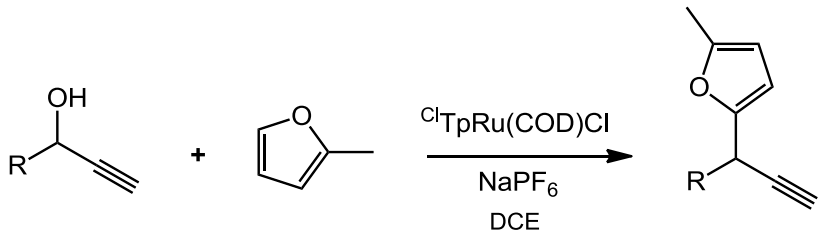


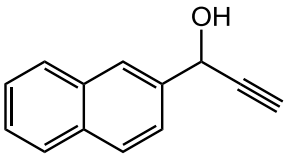
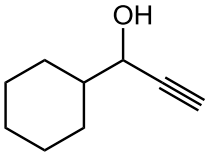
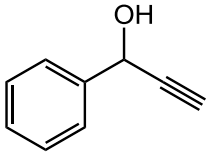
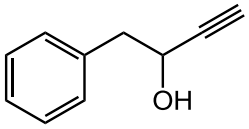
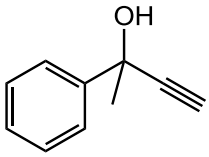
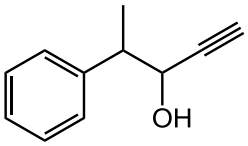
Figure 2.2.2.1 ORTEP drawing of complex **58** with 50 % probability ellipsoids. H atoms have been omitted for clarity.

2.2.3 Propargylic Substitution Reactions

The propargylation activity was first examined using 2-naphthyl propargylic alcohol with different nucleophiles (Table 2.2.3.1). Interestingly, the catalytic activity was dramatically improved when compared to TpRu(COD)Cl, possible due to the enhanced electrophilicity on the γ-carbon of the allenylidene intermediate (entry 1). The phenyl propargylic alcohol was also transformed to the corresponding product in a good yield (entry 2). Then the scope of the substrates was explored with a quaternary propargylic alcohol which shows low reactivity with other catalysts in propargylic substitution. Unfortunately, the catalytic activity was very low and altering several reaction conditions (catalyst loading, different solvents) did not improve the catalytic activity (entry 3).

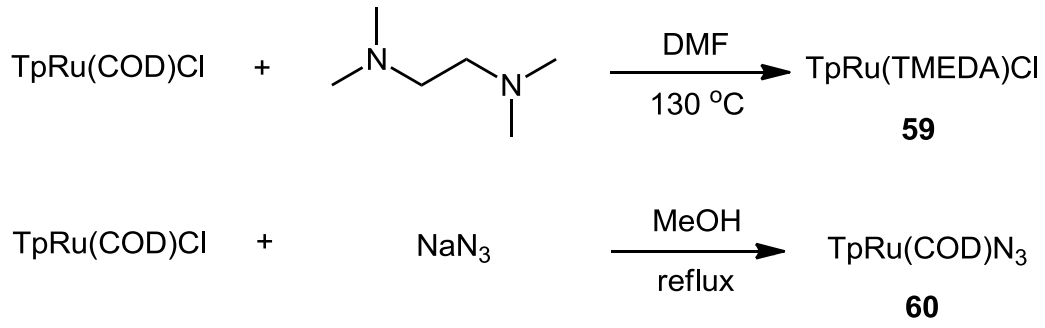
Table 2.2.3.1. The Propargylic Substitution Reactions with Catalyst **58**.



Entry	propazylic alcohol	yield	Entry	propazylic alcohol	yield
1		86 %	4		0
2		82 %	5		0
3		< 5 %	6		0

In addition, aliphatic substrates such as cyclohexyl propargylic alcohol were examined with the catalyst. However, no desired products were isolated, but the complexes which were not characterized were detected by ^{1}H NMR. This result led us to explore different ruthenium complexes (**59** and **60)** in which the ligands were changed (Scheme 2.2.3.1). Their catalytic activities were examined with aliphatic propargylic alcohols. However, they did not afford the desired products.

Scheme 2.2.3.1. The Synthesis of TpRu(TMEDA)Cl **59** and TpRu(COD)N_3, **60.**



In summary, the mononuclear ruthenium complex, ^{Cl}TpRu(COD)Cl was synthesized by a very simple method from TpRu(COD)Cl. The catalytic activity for propargylic substitution reactions with aromatic propargylic alcohols was good, but the substrate scope was very limited.

2.3 Experimental Sections

2.3.1 Materials and Methods

Reactions were performed in flame-dried glassware under an argon atmosphere using purified and purged solvents. All other reagnets were used as received from commercial sources. Reaction temperatures were controlled by an Opti Chem Digital Hotplate stirrer with temperature modulator. 1H NMR spectra were recored on JEOL NMR spectrometer (at 400 and 500 MHz) and are internally referenced to the chloroform peak (7.26 ppm relative to Me_4Si). Date for 1H NMR spectra is reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration, X-ray diffraction data are reported by 2θ vs. intensity.

2.3.2 Synthetic Procedures

2.3.2.1 Monoruthenium Complexes

$[RuCl_2(COD)]_X$ 53. To trichlororuthenium(III) trihydrate (2000 mg, , 9.64 mmol) in 40 mL ethanol at room temperature was added 1,5-cyclooctadiene (4.0 mL, 19 mmol).[29] Refluxing the solution for 24 h resulted in the separation of brown precipitates from solution. The reaction mixture was cooled to room temperature and filtered washing with diethyl ether (3 mL). The resulting brown solid was quickly transferred to round bottom flask and dried with vacuum.

[Ru(COD)H($NH_2NMe)_3$][BPF_4] 57. To [$RuCl_2$(COD)]$_X$ (2000 mg) in 25 mL methanol at room temperature was added anhydrous N,N-dimethyl hydrazine (25 mL) and water (5 mL). Refluxing the solution for 20 min and the addition of Na[BPh_4] (2.5 g) in methanol (15 mL) resulted in the formation of a dark brown solution. The addition of an aqueous solution of Na[BPh_4] (0.5 g) in methanol (15 mL) gave the precipitate as colorless plates.The reaction mixture was cooled to room temperature and filtered washing with diethyl ether (5 mL). The resulting colorless solid was transferred to round bottom flask and dried with vacuum.

[TpRu(COD)Cl] 54. To [Ru(COD)H($NH_2NMe)_3$][BPF_4] and KTp was added anhydrous acetone (30 mL). The reaction mixture was refluxed for 2 h and added CCl_4 (7 mL). After refluxed further for 30 min, the reaction mixture was cooled to -20 ^oC and KCl was removed by filtration. The resulting solution was concentrated and dried with vacuum.

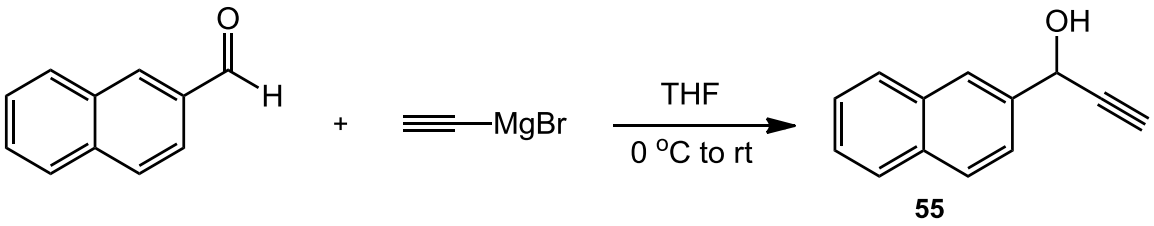
[^{Cl}TpRu(COD)Cl] 58. To TpRu(COD)Cl (568 mg, 1. 25 mmol) in 10 mL of THF was added sulfuryl chloride (1.0 mL, 12 mmol). The color of the reaction mixture was immediately changed to dark red solution. After stirring for 6 h at room temperature, the solution was concentrated and separated by column chromatography with 20 % ethyl acetate in hexane.

[TpRu(TMEDA)Cl] 59. To a solution of TpRu(COD)Cl (300 mg, 0.658 mmol) in 30mL DMF was added tetramethyldiamine (0.50 ml, 3.29 mmol) and the mixture was heated at 130 ^oC for 2 h.[30] After removal of the solvent, the resulting solid was dissolved in 15 mL

CH_2Cl_2 and insoluble materials were removed by filtration. The addition of diethyl ether afforded a yellow precipitate then washed with diethyl ether (2 x 10 mL)

[TpRu(COD)N_3] 60. To a solution of TpRu(COD)Cl (200 mg, 0.438 mmol) in 50 mL of MeOH was added excess NaN_3 (285 mg, 4.38 mmol). The solution was heated to reflux for 24 h. After cooling, the precipitates were filtered off and washed with CH_2Cl_2 and hexane. The brown solid was dried under vacuum.

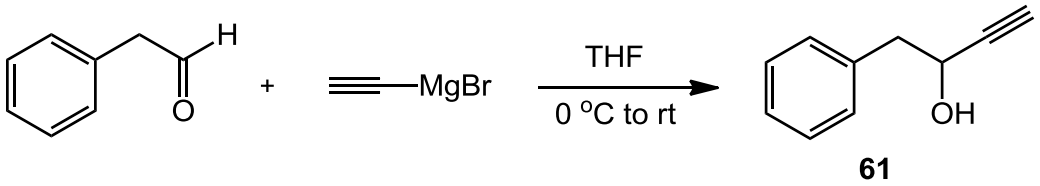
2.3.2.2 Propargylic Alcohols



55

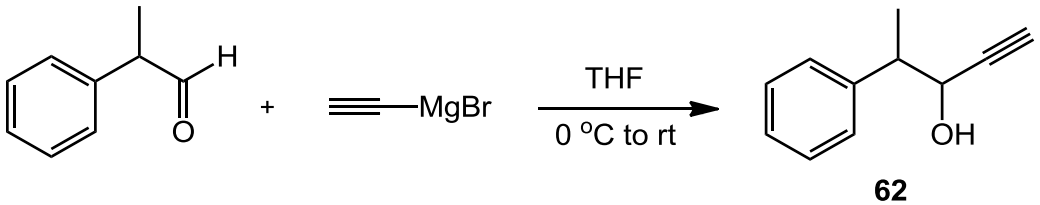
[1-(Naphthalen-2-yl)prop-2-yn-1-ol] 55. A flame-dried flask (25 mL) equipped with a Teflon stir-bar was charged with 2-naphthaldehyde (500 mg, 3.2 mmol) in 16 mL of THF. Ethynylmagnesium bromide (0.5 M in THF, 7. 68 ml, 3.84 mmol) was then added at 0 ^oC, and the solution was warmed to room temperature. After stirring for 4 h, saturated NH_4Cl was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate three times, and the combined organic layers were dried over Na_2SO_4. After filtration and concentration, this solid was purified by flash column chromatography (20 % ethyl acetate in hexane) to yield 1-(naphthalene-2-yl)prop-2-yn-1-ol (476 mg, 79 %); R_F 0.40 (20 % ethanol in hexane). ^1H NMR (400 MH_Z, $CDCl_3$) δ 8.01 (m, 1H), δ 7.86 (m, 4H), δ

7.65 (d, J = 9.6 H_Z, 1H), δ 7.51 (dd, J = 6.6 H_Z, 1H), δ 5.64 (s, 1H), δ 2.73 (d, J = 7.0 H_Z, 1H).



61

[1-Phenylbut-3-yn-2-ol] 61. A flame-dried flask (100 mL) equipped with a Teflon stir-bar was charged with phenylacetaldehyde (1000 mg, 8.32 mmol) in 32 mL of THF. Ethynylmagnesium bromide (0.5 M in THF, 20 mL, 10 mmol) was then added at 0 °C, and the solution was warmed to room temperature. After stirring for 6 h, saturated NH_4Cl was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate three times and the combined organic layers were dried over Na_2SO_4. After filtration and concentration, this solid was purified by flash column chromatography (20 % ethyl acetate in hexane) to yield product.

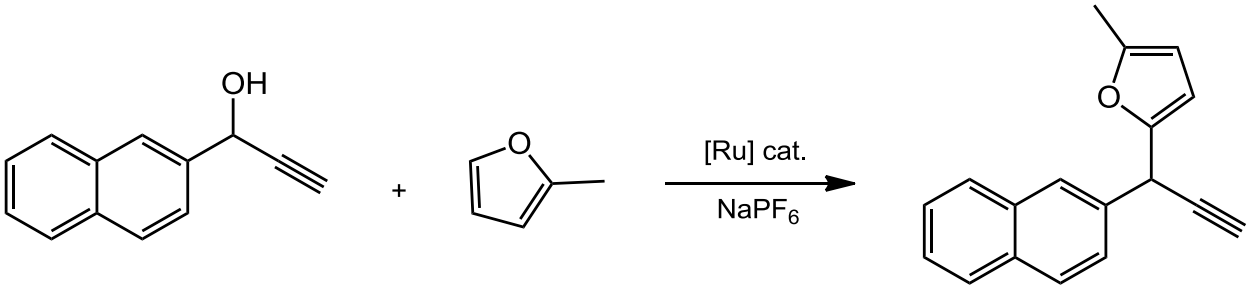


62

[4-Phenylpent-1-yn-3-ol] 62. A flame-dried flask (100 ml) equipped with a Teflon stir-bar was charged with 2-phenylpropanal (1000 mg, 7.45 mmol) in 32 mL of THF.

Ethynylmagnesium bromide (0.5 M in THF, 30 mL, 14.90 mmol) was then added at 0 ^{o}C, and the solution was warmed to room temperature. After stirring for 6 h, saturated NH_4Cl was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate three times and the combined organic layers were dried over Na_2SO_4. After filtration and concentration, this solid was purified by flash column chromatography (20 % ethyl acetate in hexane) to yield product.

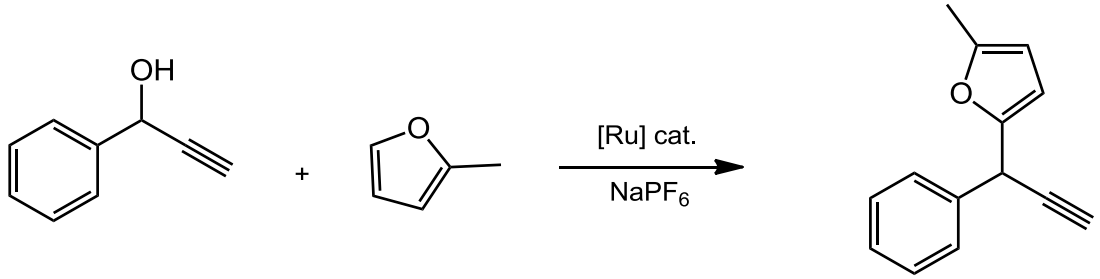
2.3.2.3 Propargylic Substitution Reactions



63

[2-(1-(Naphthalen-2-yl)prop-2-ynyl)furan] 63. A flame-dried flask (25 mL) equipped with a Teflon stir-bar was charged with 1-(naphthalene-2-yl)prop-2-yn-1-ol (25 mg, 0,17 mmol) and $NaPF_6$ (6 mg, 0.03 mmol) in 2.5 mL DCE . [^{Cl}TpRu(COD)Cl] (5 mg, 0.02 mmol) was then added at room temperature. After refluxing for 12 h, brine was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate three times and the combined organic layers were dried over Na_2SO_4. After filtration and concentration, the mixture was purified by flash column chromatography (20 % ethyl acetate in hexane)

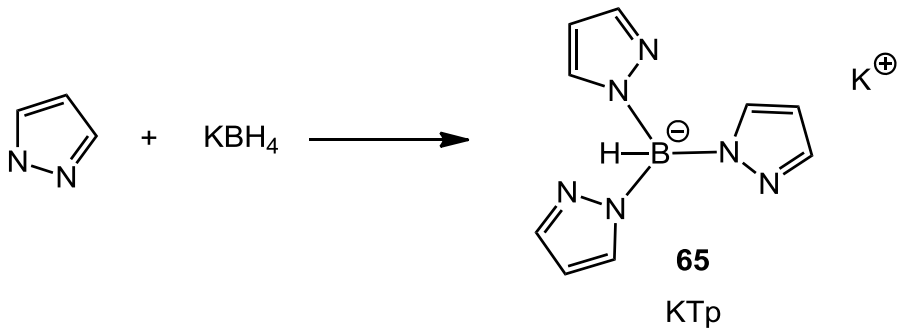
to yield 2-methyl-5-(1-(naphthalene-2-yl)prop-2-ynyl)furan. ^{1}H NMR δ = 2.24 (s, 3H), 2.45 (d, J = 2.4 Hz, 1 H), 5.70 (d, J = 2.0 Hz, 1 H), 5.87 (d, J= 2.4 Hz, 1 H), 6.03 (d, J = 3.6 Hz, 1 H), 7.44–7.53 (m, 3 H), 7.62 (d, J = 6.8 Hz, 1 H), 7.80 (d, J = 8.4 Hz, 1 H), 7.86 (d, J = 8.0 Hz,1 H), 8.12 (d, J = 8.4 Hz, 1 H) ppm.



64

[2-(1-Phenylprop-2-ynyl)furan] 64. A flame-dried flask (25 mL) equipped with a Teflon stir-bar was charged with 1-phenylprop-2-yn-1-ol (25 mg, 0,186 mmol) and $NaPF_6$ (6.0 mg, 0.03 mmol) in 2.5 mL DCE . [^{Cl}TpRu(COD)Cl] (5.0 mg, 0.02 mmol) was then added at room temperature. After refluxing for 12h, brine was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate three times and the combined organic layers were dried over Na_2SO_4. After filtration and concentration, the mixture was purified by flash column chromatography (20 % ethyl acetate in hexane) to yield (1-(4-methylcyclopenta-1,3-dienyl)prop-2-ynyl)benzene. ^{1}H NMR δ = 2.23 (s, 3 H), 2.41 (d, J = 3.0 Hz, 1 H), 5.00 (s,1 H), 5.88 (s, 1 H), 6.06 (d, J = 3.0 Hz, 1 H), 7.25–7.43 (m, 5 H)

2.3.2.4 Ligands



[KTp] 65. A flame-dried flask (25 ml) equipped with a Teflon stir-bar was charged with pyrazole (10.0 g, 104 mmol) and KBH_4 (1.40 g, 26 mmol). After heated for 4 h at 180 ^{o}C, the white residue was washed with hot toluene (10 mL) and hexane (10 mL) and dried.

2.4 References

[26] "Ruthenium-Catalyzed Enantioselective Propargylic of Aromatic Compounds with Propargylic Alcohols via Allenylidene Intermediates." Kuninobu, Y.; Ishii, E.; Takai, K. *Angew. Chem. Int. Ed*. **2007**, *46*, 3296–3299.

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[28] "Ruthenium Tris(pyrazolyl)borate Complexes. 1. Synthesis and Reactivity of $Ru(HB(pz)_3))(COD)X$ (X= Cl, Br) and $Ru(HB(pz)_3)(L)_2Cl$ (L= Nitrogen and Phosphorus Donor Ligands)." Gemel, C.; Trimmel, G.; Slugovc, C.; Kremel, S.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics*, **1996**, *15*, 3998–4004.

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[30] "Hydride, Dihydrogen, Dinitrogen and Related Complexes of Ruthenium Containing the Ligand Hydrotris(pyrazolyl)borate" Tenorio, M. J.; Jimenez Tenorio, M. A.; Puerta, M. C.; Valerga, P. *Inorg. Chim. Acta*. **1997**, *259*, 77–79

2.5 X-Ray Crystal Structure Analysis

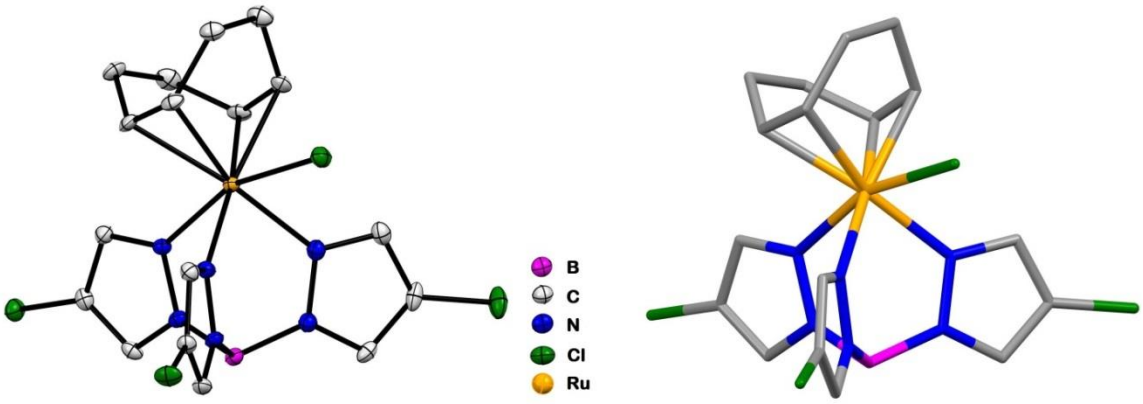


Table 2.5.1. Crystal Data and Structure Refinement for **58**.

Identification code: Compound **58**

Empirical formula: $C_{17}\ H_{19}\ B\ Cl_4\ N_6\ Ru$

Formula weight: 561.06

Temperature: 100(2) K

Wavelength: 0.71073 A

Crystal system, space group: Triclinic, P-1

Unit cell dimensions a = 7.9212(7) A alpha = 95.929(1) deg.
b = 8.1305(8) A beta = 91.185(1) deg.
c = 15.7484(15) A gamma = 92.510(1) deg.

Volume: 1007.53(16) A^3

Z, Calculated density: 2, 1.849 Mg/m^3

Absorption coefficient: 1.327 mm^-1

F(000): 560

Crystal color and shape: Orange block

Crystal size: 0.25 x 0.20 x 0.20 mm

Theta range for data collection: 1.30 to 26.00 deg.

Limiting indices: -9<=h<=9, -10<=k<=9, 0<=l<=19

Reflections collected / unique: 5987 / 3899 [R(int) = 0.0456]

Completeness to theta = 26.00, 98.5 %

Absorption correction: Empirical

Max. and min. transmission: 0.9767 and 0.7200

Refinement method: Full-matrix least-squares on F^2

Data / restraints / parameters: 3836 / 0 / 266

Goodness-of-fit on F^2: 1.894

Final R indices [I>4sigma(I)]: R1 = 0.0253, wR2 = 0.0724

R indices (all data): R1 = 0.0347, wR2 = 0.1158

Extinction coefficient: 0.0071(17)

Largest diff. peak and hole: 0.887 and -0.883 e.A^-3

Table 2.5.2 Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (A^2 x 10^3) for **58**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ru	4142(1)	6415(1)	2865(1)	10(1)
Cl(1)	5878(1)	4533(1)	3554(1)	16(1)
Cl(2)	6490(1)	2100(1)	-98(1)	23(1)
Cl(3)	-546(1)	2141(1)	4663(1)	19(1)
Cl(4)	-1099(1)	9999(1)	1046(1)	17(1)
B(1)	1259(5)	4253(5)	1709(3)	13(1)
N(1)	4403(4)	4647(4)	1790(2)	14(1)
N(2)	3033(4)	3816(4)	1404(2)	13(1)
N(3)	2160(4)	4872(4)	3264(2)	13(1)
N(4)	1115(4)	3990(4)	2658(2)	12(1)
N(5)	2089(4)	7299(4)	2131(2)	12(1)
N(6)	1103(4)	6115(4)	1636(2)	12(1)
C(1)	5752(5)	4167(5)	1356(3)	16(1)
C(2)	5220(5)	3025(5)	671(3)	17(1)
C(3)	3499(5)	2824(5)	719(2)	14(1)
C(4)	1754(5)	4372(5)	4016(3)	14(1)
C(5)	426(5)	3177(5)	3894(2)	13(1)
C(6)	36(5)	2959(5)	3030(3)	14(1)
C(7)	1458(5)	8758(5)	2010(2)	13(1)
C(8)	81(5)	8497(5)	1420(3)	14(1)
C(9)	-89(5)	6829(5)	1206(2)	13(1)
C(10)	5654(5)	8285(5)	2228(3)	15(1)
C(11)	6722(5)	7505(5)	2749(3)	15(1)
C(12)	7497(5)	8347(6)	3583(3)	19(1)
C(13)	6384(5)	8175(5)	4373(3)	17(1)
C(14)	4541(5)	7794(5)	4162(2)	14(1)
C(15)	3577(5)	8737(5)	3669(2)	14(1)
C(16)	4348(5)	10321(5)	3348(3)	16(1)

C(17)	5155(5)	10041(5)	2459(3)	18(1)

Table 2.5.3. Bond Lengths [A] and Angles [deg] for **58**.

Ru-N(3)	2.113(3)
Ru-N(1)	2.124(3)
Ru-N(5)	2.167(3)
Ru-C(11)	2.210(4)
Ru-C(10)	2.227(4)
Ru-C(15)	2.230(4)
Ru-C(14)	2.235(4)
Ru-Cl(1)	2.4238(10)
Cl(2)-C(2)	1.724(4)
Cl(3)-C(5)	1.721(4)
Cl(4)-C(8)	1.714(4)
B(1)-N(4)	1.537(5)
B(1)-N(2)	1.539(5)
B(1)-N(6)	1.541(5)
N(1)-C(1)	1.331(5)
N(1)-N(2)	1.352(5)
N(2)-C(3)	1.347(5)
N(3)-C(4)	1.332(5)
N(3)-N(4)	1.373(5)
N(4)-C(6)	1.354(5)
N(5)-C(7)	1.337(5)
N(5)-N(6)	1.378(5)
N(6)-C(9)	1.338(5)
C(1)-C(2)	1.394(6)
C(2)-C(3)	1.371(6)
C(4)-C(5)	1.396(5)
C(5)-C(6)	1.381(6)
C(7)-C(8)	1.413(5)

Table 2.5.3. Bond Lengths [A] and Angles [deg] for **58**.

C(11)-C(12)	1.522(6)
C(12)-C(13)	1.554(6)
C(13)-C(14)	1.502(6)
C(14)-C(15)	1.386(6)
C(15)-C(16)	1.538(5)
C(16)-C(17)	1.551(6)
N(3)-Ru-N(1)	88.18(13)
N(3)-Ru-N(5)	81.54(12)
N(1)-Ru-N(5)	85.26(12)
N(3)-Ru-C(11)	159.54(14)
N(1)-Ru-C(11)	92.70(14)
N(5)-Ru-C(11)	118.91(14)
N(3)-Ru-C(10)	164.10(14)
N(1)-Ru-C(10)	90.19(14)
N(5)-Ru-C(10)	82.56(14)
C(11)-Ru-C(10)	36.35(15)
N(3)-Ru-C(15)	98.24(14)
N(1)-Ru-C(15)	161.74(14)
N(5)-Ru-C(15)	78.87(14)
C(11)-Ru-C(15)	87.21(15)
C(10)-Ru-C(15)	78.96(15)
N(3)-Ru-C(14)	93.30(13)
N(1)-Ru-C(14)	161.10(14)
N(5)-Ru-C(14)	113.61(14)
C(11)-Ru-C(14)	79.46(15)
C(10)-Ru-C(14)	93.35(14)
C(15)-Ru-C(14)	36.17(15)
N(3)-Ru-Cl(1)	82.50(9)
N(1)-Ru-Cl(1)	82.38(9)
N(5)-Ru-Cl(1)	160.07(9)
C(11)-Ru-Cl(1)	77.37(11)
C(10)-Ru-Cl(1)	112.96(11)

Table 2.5.3. Bond Lengths [A] and Angles [deg] for **58**.

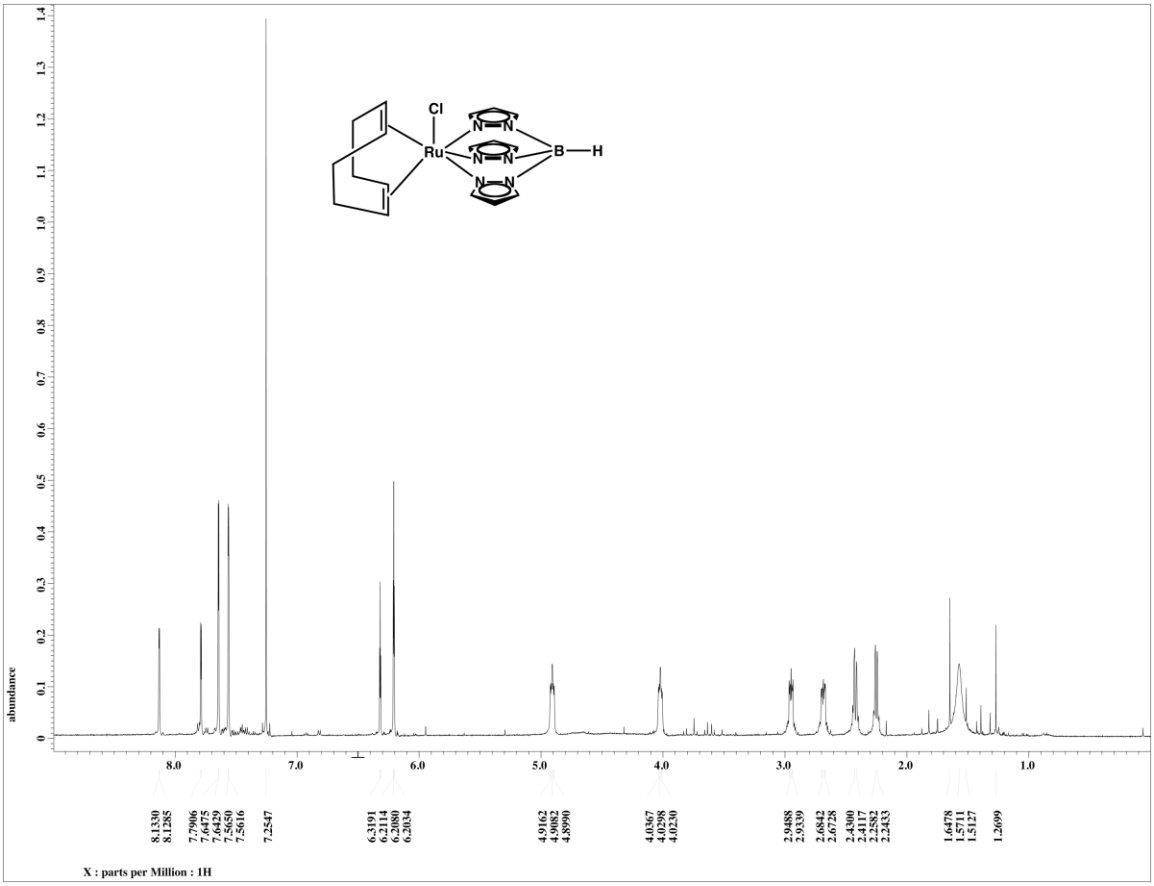
N(4)-B(1)-N(6)	107.4(3)
N(2)-B(1)-N(6)	106.6(3)
C(1)-N(1)-N(2)	107.5(3)
C(1)-N(1)-Ru	131.7(3)
N(2)-N(1)-Ru	120.8(2)
C(3)-N(2)-N(1)	110.2(3)
C(3)-N(2)-B(1)	130.0(3)
N(1)-N(2)-B(1)	119.3(3)
C(4)-N(3)-N(4)	107.0(3)
C(4)-N(3)-Ru	133.4(3)
N(4)-N(3)-Ru	119.0(2)
C(6)-N(4)-N(3)	110.3(3)
C(6)-N(4)-B(1)	129.0(3)
N(3)-N(4)-B(1)	120.7(3)
C(7)-N(5)-N(6)	106.4(3)
C(7)-N(5)-Ru	137.1(3)
N(6)-N(5)-Ru	116.5(2)
C(9)-N(6)-N(5)	110.3(3)
C(9)-N(6)-B(1)	127.3(3)
N(5)-N(6)-B(1)	121.8(3)
N(1)-C(1)-C(2)	108.7(4)
C(3)-C(2)-C(1)	106.6(4)
C(3)-C(2)-Cl(2)	127.2(3)
C(1)-C(2)-Cl(2)	126.2(3)
N(2)-C(3)-C(2)	107.0(3)
N(3)-C(4)-C(5)	109.1(3)
C(6)-C(5)-C(4)	107.1(3)
C(6)-C(5)-Cl(3)	125.8(3)
C(4)-C(5)-Cl(3)	127.2(3)
N(4)-C(6)-C(5)	106.5(3)
N(5)-C(7)-C(8)	109.1(3)
C(9)-C(8)-C(7)	106.1(3)
C(9)-C(8)-Cl(4)	127.7(3)
C(7)-C(8)-Cl(4)	126.2(3)

Table 2.5.3. Bond Lengths [A] and Angles [deg] for **58**.

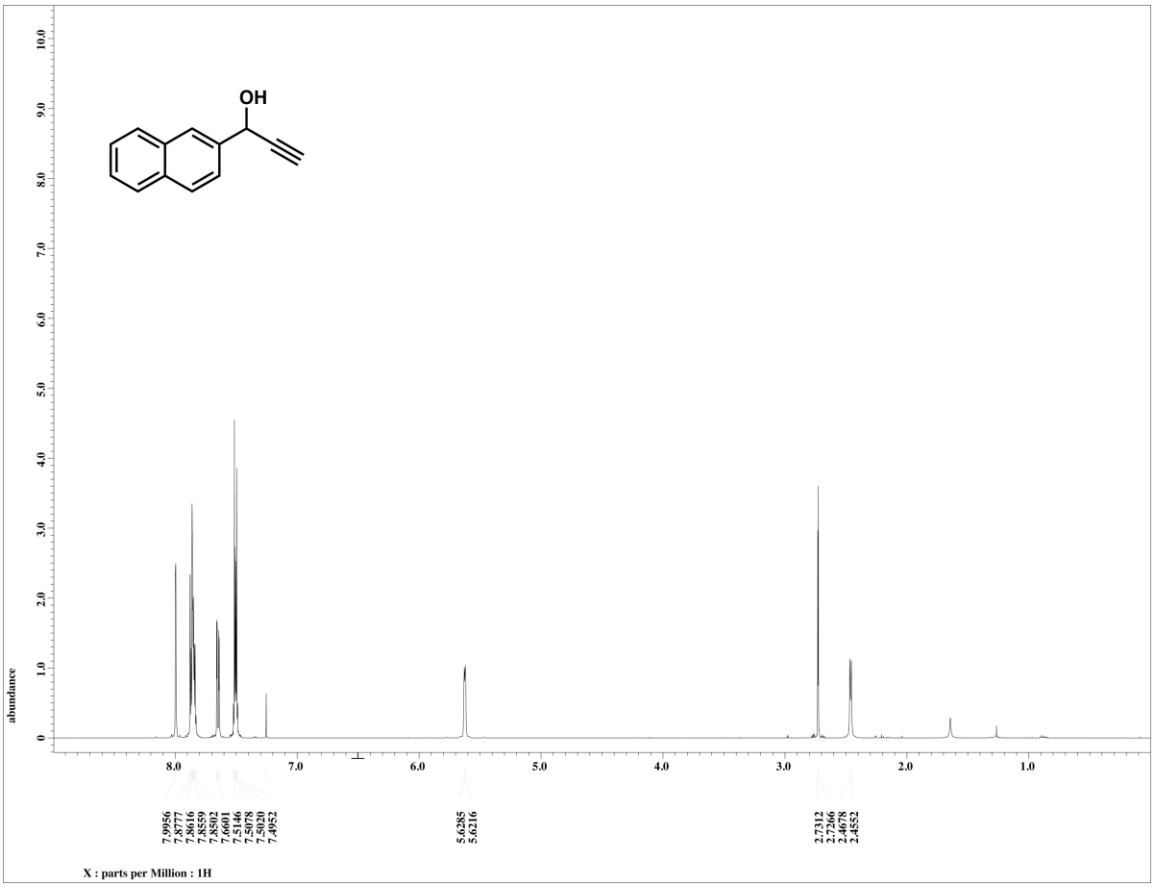
C(17)-C(10)-Ru	113.8(3)
C(10)-C(11)-C(12)	123.0(4)
C(10)-C(11)-Ru	72.5(2)
C(12)-C(11)-Ru	114.2(3)
C(11)-C(12)-C(13)	114.1(3)
C(14)-C(13)-C(12)	114.3(3)
C(15)-C(14)-C(13)	123.4(4)
C(15)-C(14)-Ru	71.7(2)
C(13)-C(14)-Ru	111.8(3)
C(14)-C(15)-C(16)	120.4(4)
C(14)-C(15)-Ru	72.1(2)
C(16)-C(15)-Ru	114.1(3)
C(15)-C(16)-C(17)	114.1(3)
C(10)-C(17)-C(16)	113.5(3)

2.6 ^{1}H NMR Data

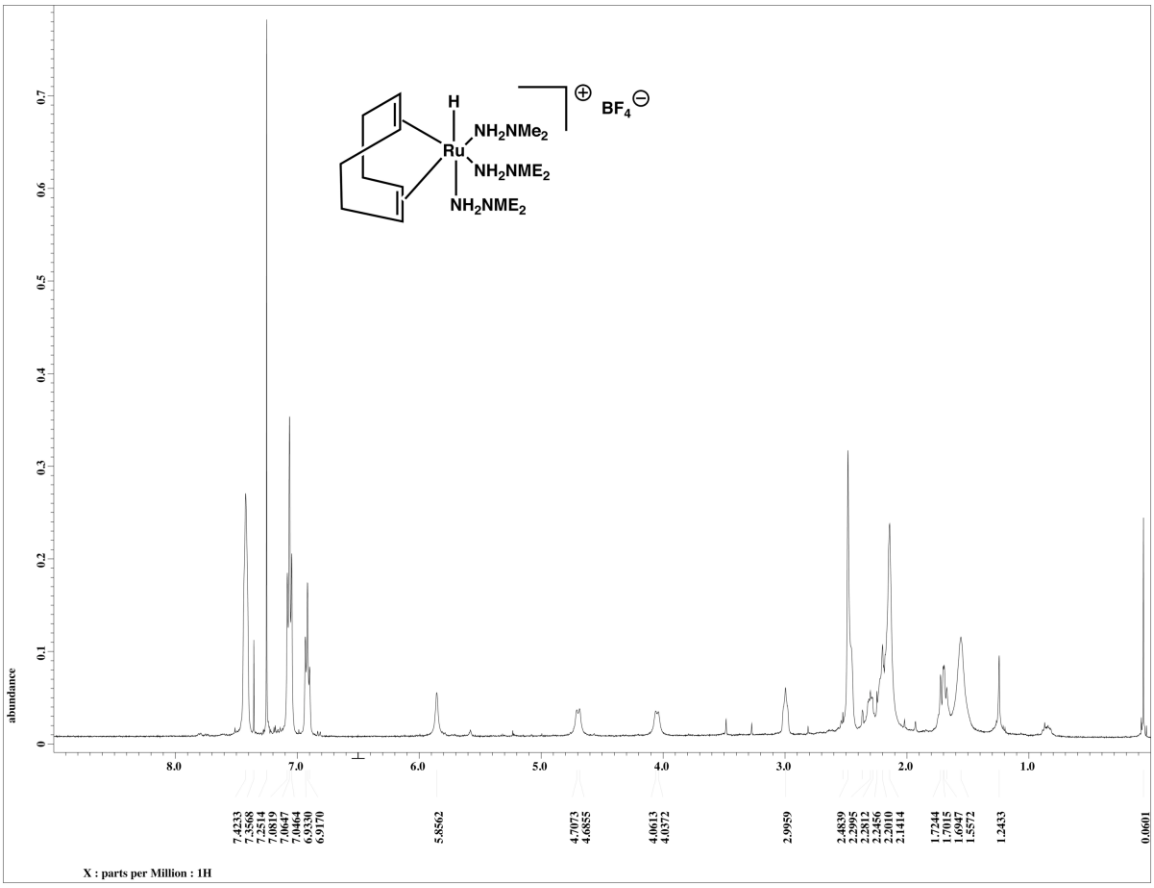
For complex 54.



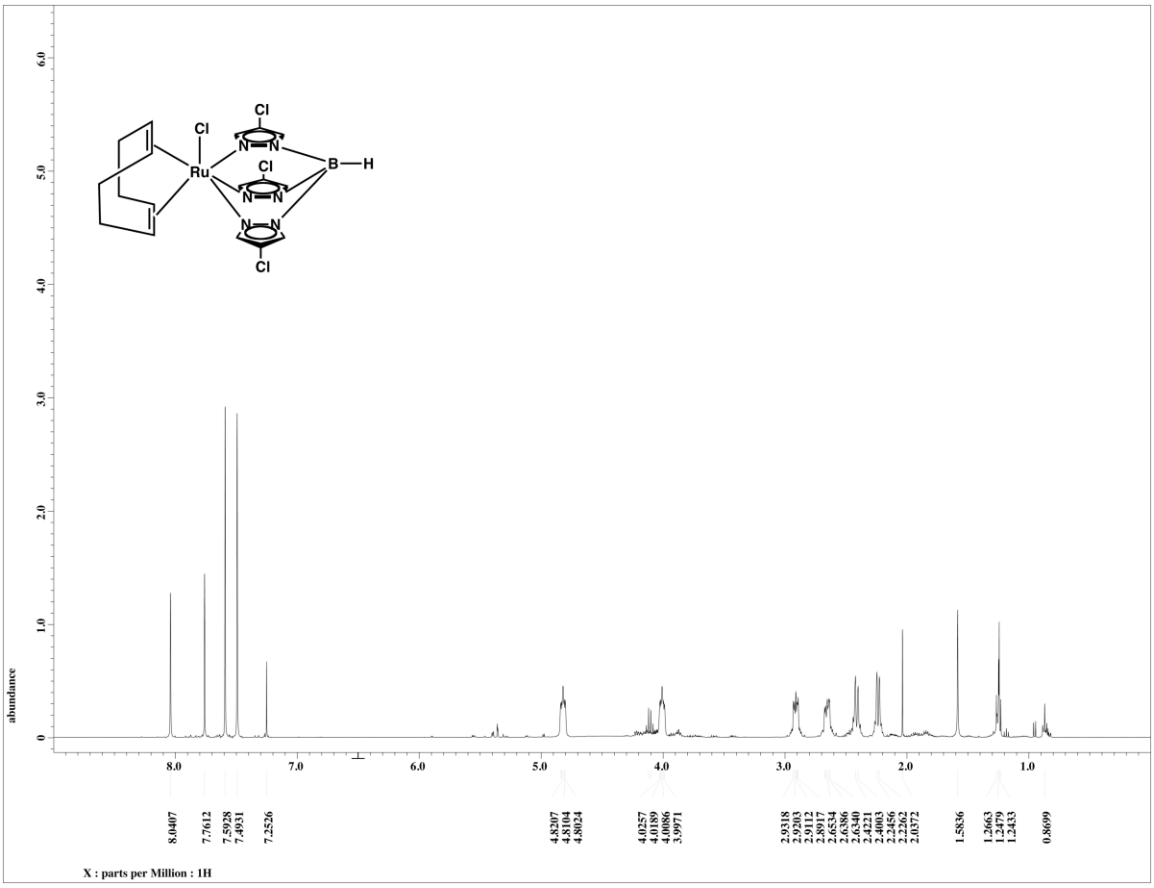
For complex 55.



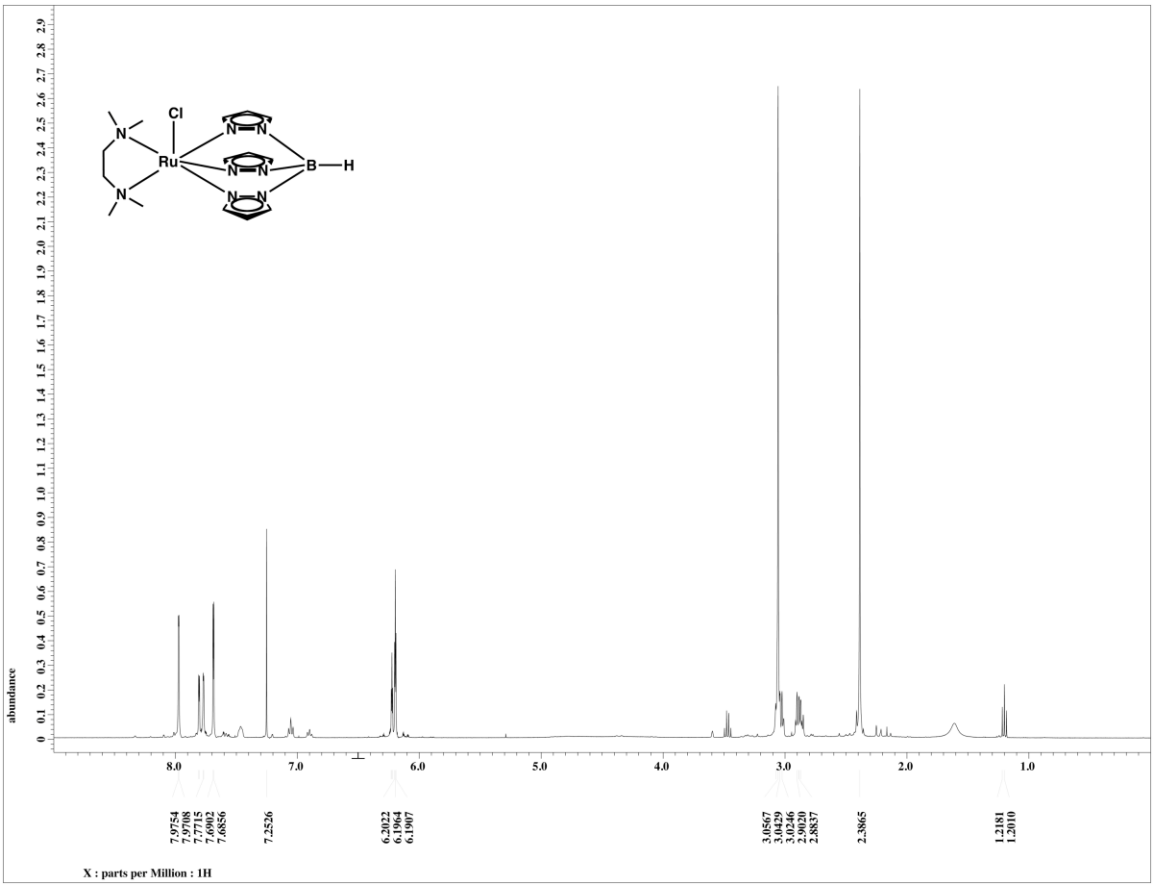
For complex 57.



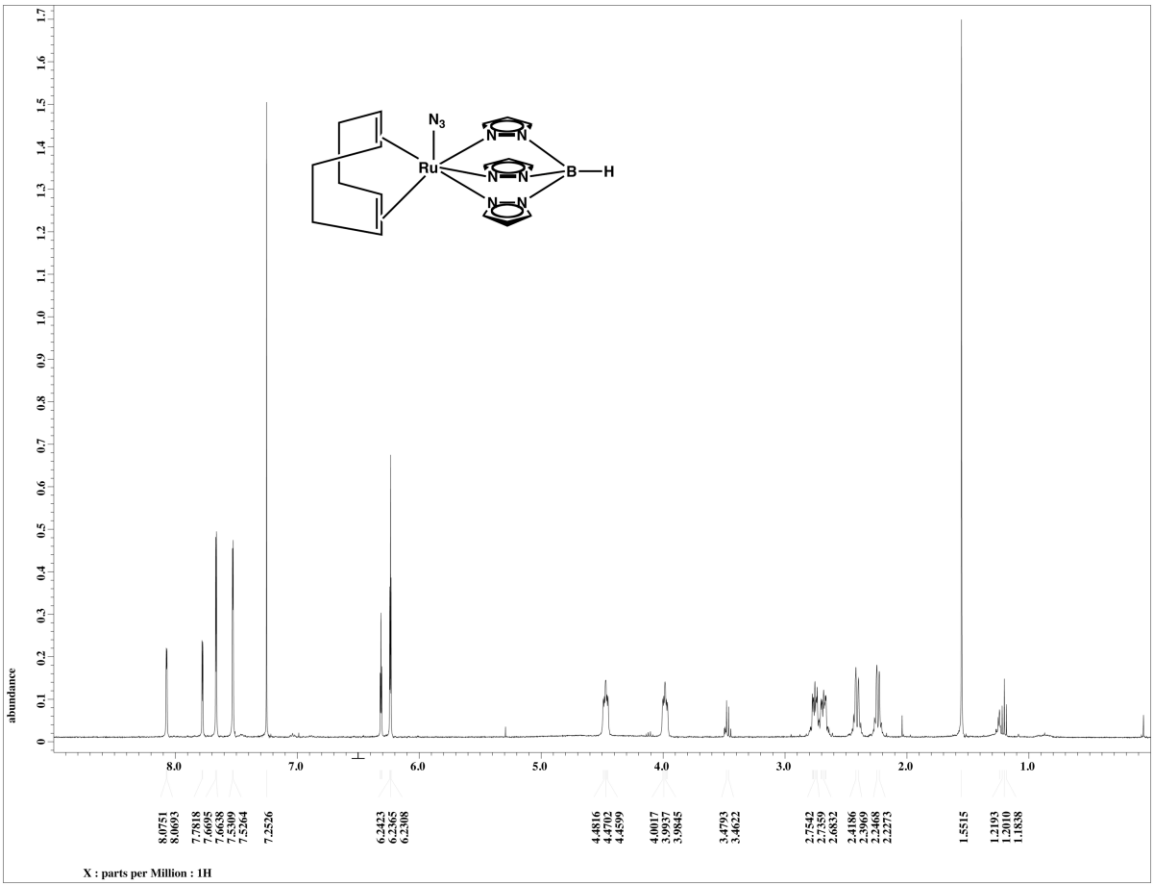
For complex 58.



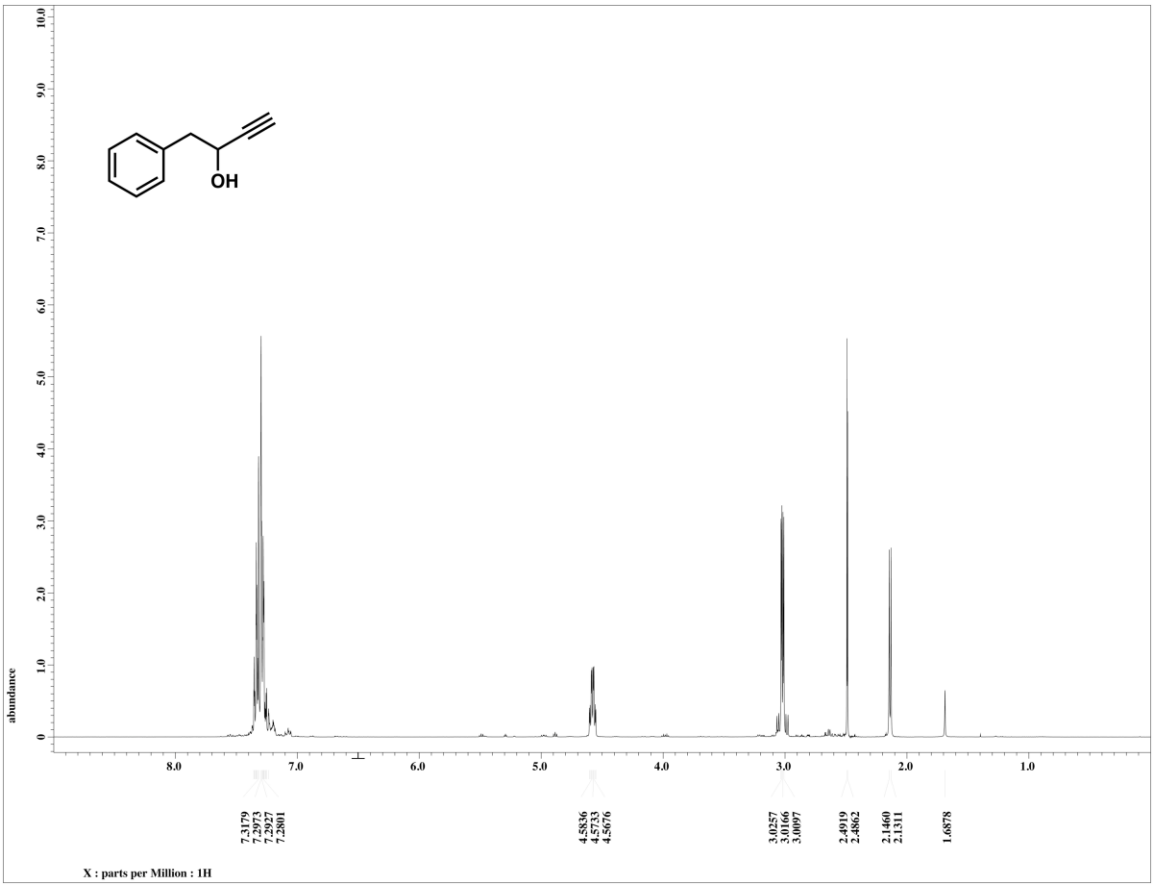
For complex 59.



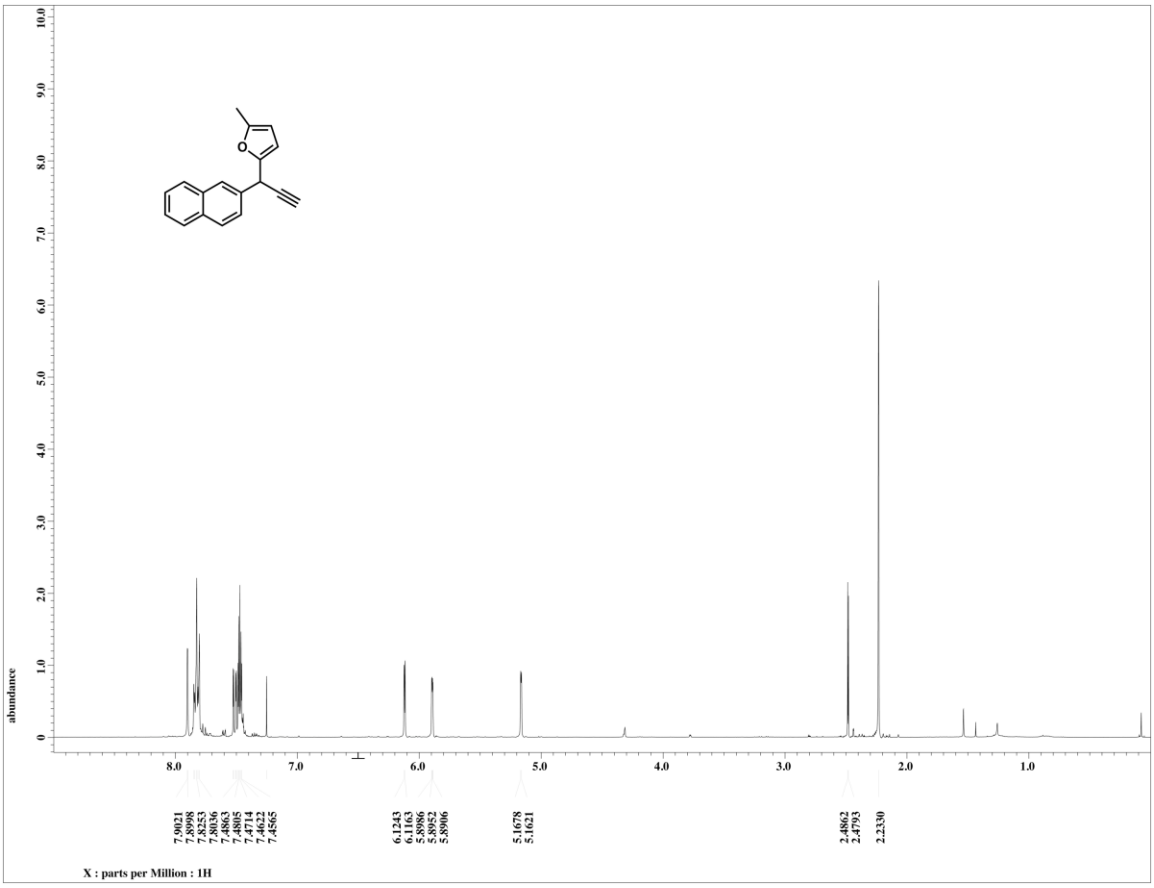
For complex 60.



For complex 61.



For complex 63.



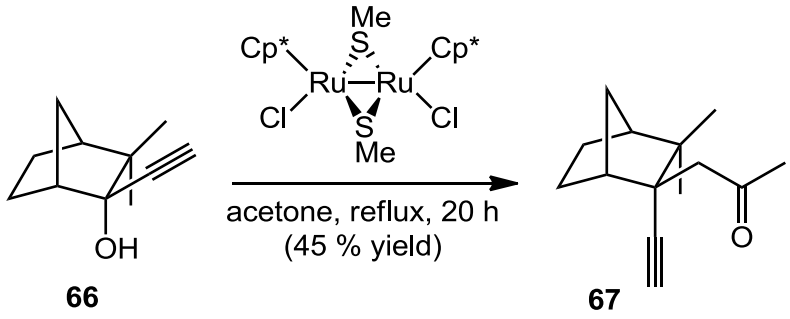
Chapter Three

Synthesis and Catalytic Activity of Diruthenium Complexes that Contain Cp Derivatives as Ligands

3.1 Background and Specific Aims

Previously reported diruthenium complexes showed catalytic activities only with 1-aryl secondary propargyl alcohols in most examples. In addition, there is only one example of a tertiary propargylic alcohol to generate a quaternary carbon center (Scheme 3.1.1).[31] Bicyclo[2.2.1]heptane **66** has no hydrogen adjacent to the propargylic carbon center. The methyl substituents are able to stabilize the allenylidene intermediate to prevent isomerization. These drawbacks were our motivation to develop novel Ru catalyst for various substrates.

Scheme 3.1.1*:* Formation of Dense Carbon Substitution.



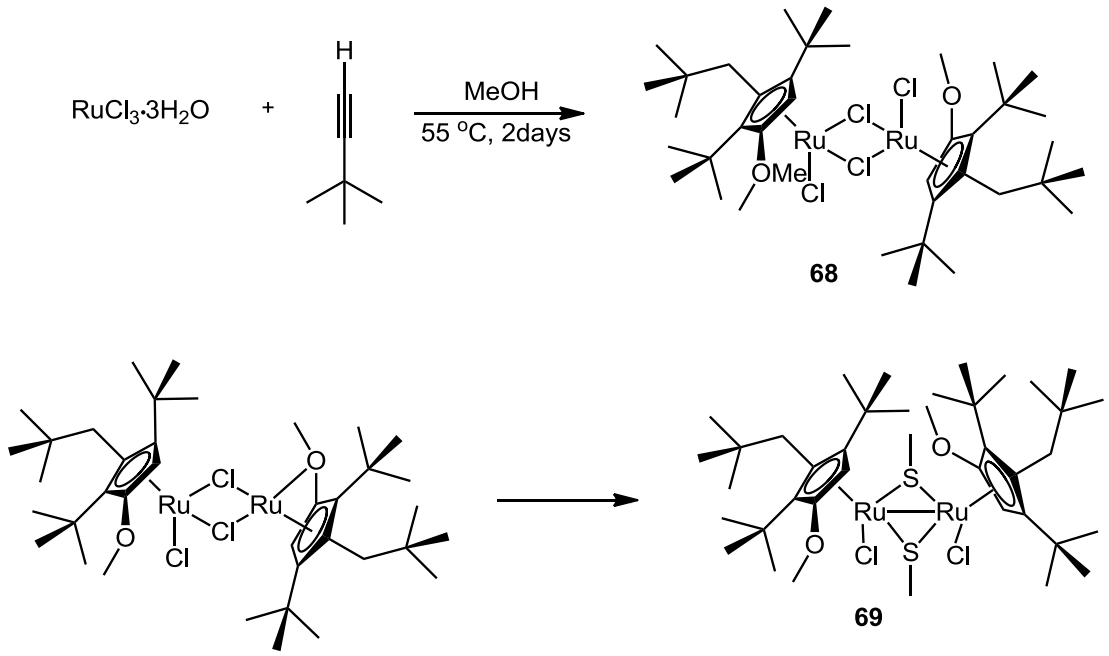
66 **67**

3.2 Results and Discussions

3.2.1 Synthesis of Diruthenium Complexes that Contain Cp Derivatives as Ligands

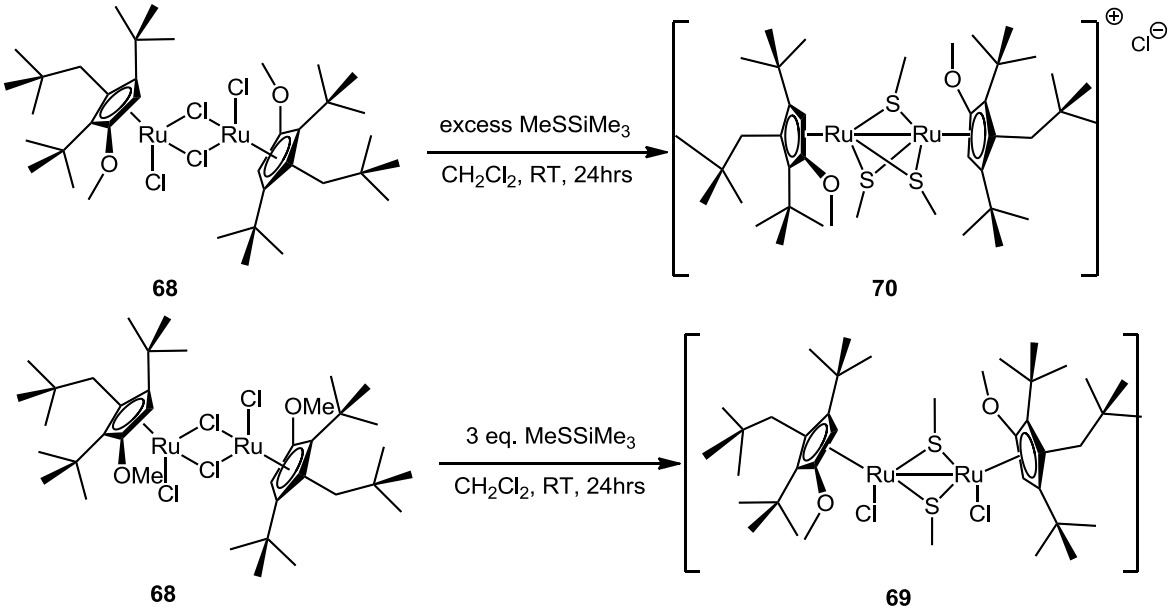
We initially pursued a goal to synthesize catalysts that perform intermolecular propargylic substitutions because current diruthenium catalysts have showed that the key allenylidene intermediate was isomerized to give vinyl-vinylidene intermediate. The introduction of sterically hindered ligands could be one way to prevent isomerization through the formation of thermodynamically favored allenylidenes. We have begun synthesizing new dual-metal complexes with modified Cp ligands starting from the half sandwich dimeric catalyst precursor **68**.[32] Though this paramagnetic complex was difficult to analyze via NMR, we used powder X-ray diffraction to characterize the structure of this and other new Cp derivatives. Next, conditions were determined to convert this complex to thiol-bridged structures like **69**. We have explored 3 different thiol sources to form them (Scheme 3.2.1.1). Fortunately, we have grown crystals from the reaction conditions ($CHCl_3$/hexane) and characterized the product structures with X-ray crystallography.

Scheme 3.2.1.1. The Formation of Thiolate-Bridged Diruthenium Complexes.



The reactions of $[Cp^{\wedge}RuCl(\mu\text{-}Cl)]_2$ **68** with $MeSSiMe_3$ in CH_2Cl_2 at room temperature afforded two types of thiolate-bridged dinuclear Ru(III) complexes. Reaction of **68** with excess $MeSSiMe_3$ in CH_2Cl_2 resulted in the formation of a triply bridged complex, $[Cp^{\wedge}Ru(\mu\text{-}SMe)_3RuCp^{\wedge}]Cl$, **70**. However, 3 equivalents of $MeSSiMe_3$ afforded a doubly bridged diruthenium complex, $[Cp^{\wedge}RuCl(\mu\text{-}SMe)_2RuCp^{\wedge}Cl]$ **69 (**Scheme 3.2.1.2**)**. Neither isopropyl thiol nor diisopropyl sulfide reacted with **68**, even when refluxed in THF. NMR and X-ray crystallography studies were undertaken for **69** and **70** to confirm their structures.

Scheme 3.2.1.2. Doubly or Triply Bridged Complexes



Complex **69** has the expected dithiolate structure, and one half of the molecule relates to the other by a crystallographically imposed C_2 axis (Figure 3.2.1.1). The Ru-Ru distance of 2.848 Å is much shorter than that of **68** (3.684 Å),[32] indicating the presence of a Ru-Ru single bond. This bond length observed for **69** is comparable to those in other thiolate-bridged Ru(III) complexes such as [Cp*RuCl(μ-SR)$_2$RuCp*Cl].

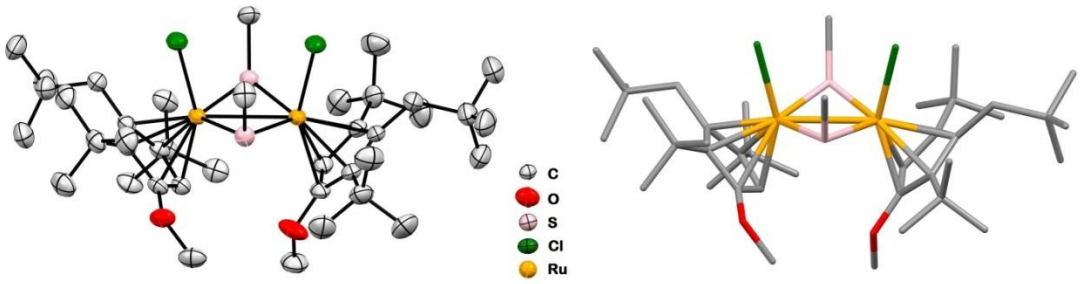


Figure 3.2.1.1.Crystal Structure of [Cp^RuCl(μ-SMe)$_2$RuCp^Cl], **69**

The structure of complex **70** was also determined by X-ray crystallography (Figure 3.2.1.2).

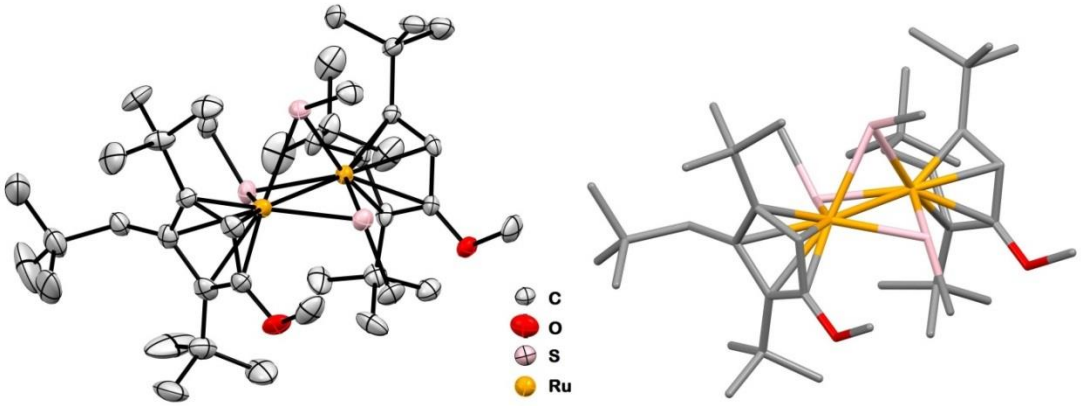
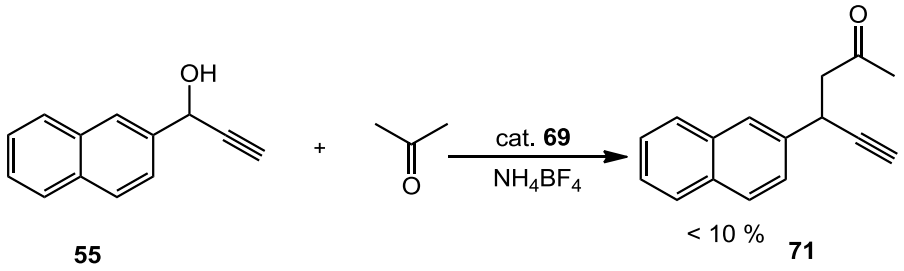


Figure 3.2.1.2.Crystal Structure of [Cp^RuCl(μ-SMe)$_3$RuCp^Cl], **70**

Next, the reaction of propargylic alcohol **55** with acetone were investigated in the presence of **69** or **70** (5 mol %) and NH_4BF_4 (10 mol %) at 60 ^oC for 12 h (Scheme 3.2.1.3). Unfortunately, the reaction afforded only trace amount of the desired product. It seems that the bulky ligands may interfere with the substrates, approach to the

allenylidine intermediate. Examination of the complex will be continued when enough of the complex is obtained to screen the reaction conditions.

Scheme 3.2.1.3. The Catalyst Test for Propargylation



3.2.2 Synthesis of Diruthenium complexes with Tp

We also investigated the use of hydrotris(pyrazolyl)borate (Tp), hydrodtris(3,5-dimethyl pyrazolyl)borate (Tp*), and hydrotris(triazolyl)borate (Ttz) ligands, which are considered to be strong donor (Tp and Tp*) or a donor (Ttz) ligands (Figure 3.2.2.1).[33] The Tp ligand and derivatives have demonstrated many similarities with their Cp analogues, but some non-parallel behaviors with respect to their reactivity.[13] The Tp ligand turns out to be versatile in a wide variety of inorganic studies, because the coordination properties (both steric and electronic) can be finely tuned by choosing appropriate substituents on the pyrazolyl ring. Those three ligands were prepared by the reaction of pyrazolyl analogues and KBH_4. In the beginning, we sought reaction conditions to generate [$TpRuCl_2$], which could be precursor to afford a doubly bridged

bimetallic complex. Despite much effort, the $TpRuCl_2$ complex has remained unattainable (Table 3.2.2.1). The reaction of $RuCl_3.3H_2O$ with KTp* in EtOH resulted in the formation of $RuCl_2(3,5\text{-}CH_3\text{-pyrazolyl})_4$ as confirmed by single crystal X-ray diffraction. On the other hand, the reaction of $Ru(COD)Cl_2$ with KTp* in THF at reflux afforded Tp*Ru(COD)Cl in which a Cl ligand was replaced by Tp*.

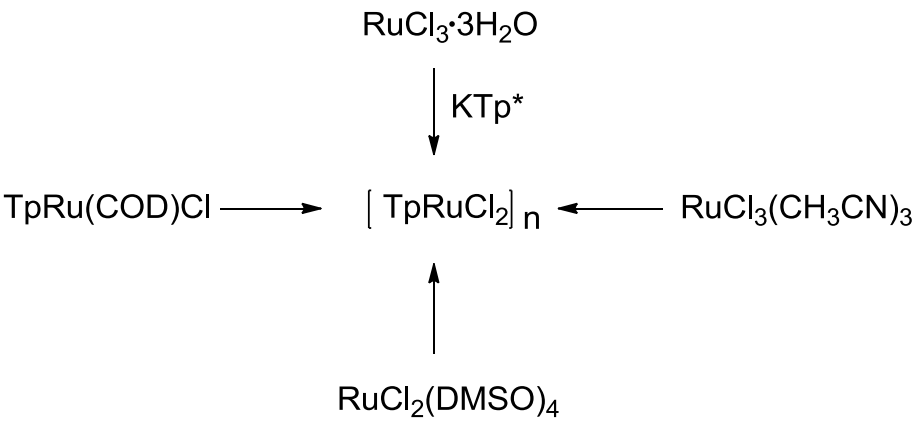


Figure 3.2.2.1. The Efforts to Synthesize $TpRuCl_2$ and Dithiolated-Bridged Complexes.

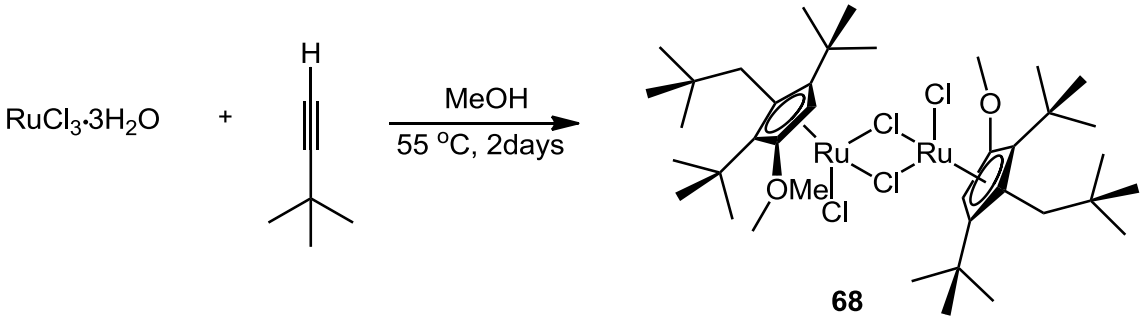
Table 3.2.2.1. Screening to Form $TpRuCl_2$

reagent	ligand	solvent	T	crystal
$RuCl_3{\cdot}3H_2O$	KTp	EtOH	70 °C	NA
$RuCl_3{\cdot}3H_2O$	KTp*	EtOH	reflux	$RuCl_2(3,5\text{-}CH_3pyr)_4$
$RuCl_3{\cdot}3H_2O$	KTp	MeOH	60 °C	NA
$RuCl_3{\cdot}3H_2O$	KTp	THF	RT	NA
$RuCl_3{\cdot}3H_2O$	KTp	CH_2Cl_2	RT	NA
$Ru(COD)Cl_2$	KTp	THF	60 °C	TpRu(COD)Cl
$RuCl_2(DMSO)_4$	KTp	THF	reflux	NA
$CuCl_2{\cdot}2H_2O$	KTp	EtOH	60 °C	TpCuCl
$CuCl_2{\cdot}2H_2O$	KTp	EtOH	60 °C	$TpRhCl_2$

In summary, thiolate-bridged diruthenium complexes were synthesized and examined for catalytic activity in the propargylic substitution reaction. These dibridged-dual ruthenium complexes will be expanded to different ligands and modified with different metals for propargylic C-C bond formation. Our long-term goal will be more efficient conversion of readily available small molecule hydrocarbons into synthetically useful species with control over regioselectivity and stereoselectivity in bond formation.

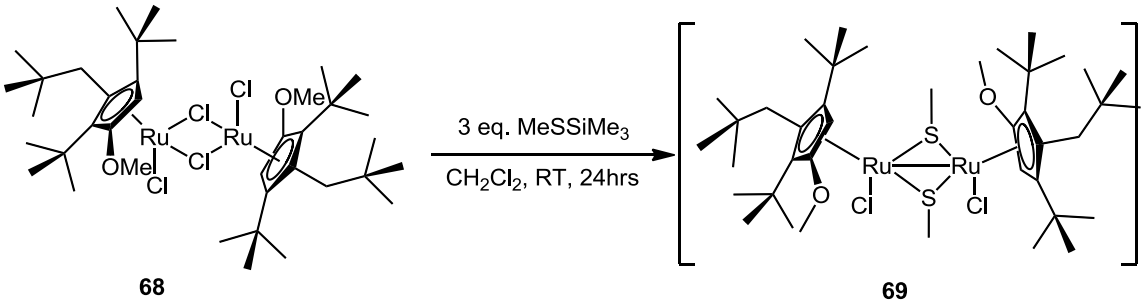
3. 3 Experimental Section

3.3.1 Diruthenium Complexes



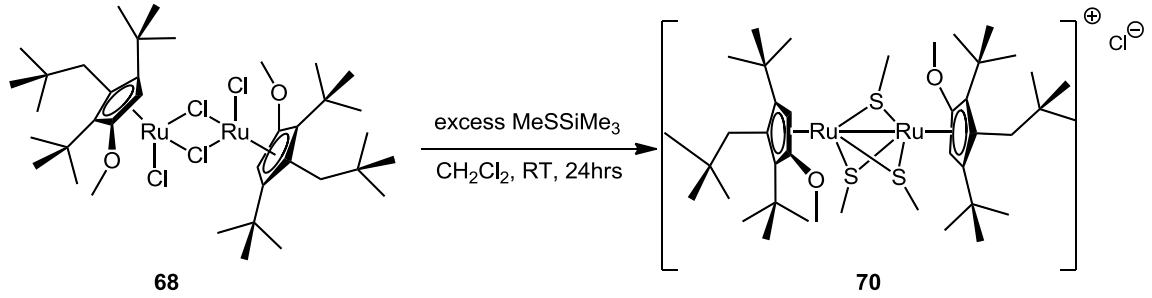
68

[Diruthenium complex] 68. To trichlororuthenium chloride(III) hydrate (2.0g, 7.7 mmol) in 40 mL methanol at room temperature was add 3,3-dimethylbut-1-yne (4.0 mL, 32 mmol).[32] Refluxing the solution for 12 h resulted in the separation of red-brown microcrystals. The reaction mixture was cooled to room temperature and then kept in -40 ^{o}C. After 24 h, the solid was filtered off, washed with ethanol, and then recrystallized from diethyl ether. The red-brown crystals were dried under vacuum to afford diruthenium complex 60 (63 %).



68 69

[Doubly Thiolate-bridged Diruthenium complexes] 69. To a suspension of complex **63** (100 mg, 0.11 mmol) in 3 ml dichloromethane was added $MeSSiMe_3$ (0.03 mL, 0.23 mmol). After stirring for 12 h at room temperature, 10 mL anhydrous hexane was added to the reaction mixture and stored at -20 ^oC. The solution was filtered off and the resulting dark brown solid was crystallized with $CHCl_3$/hexane to give single crystals (<5 %).



68 70

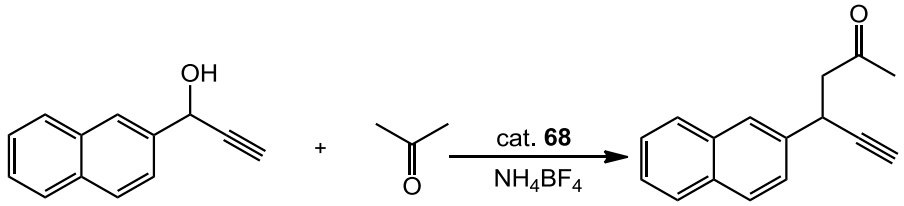
[Triply Thiolate-bridged Diruthenium Complex] 70. To a suspension of complex **68** (200 mg, 0.23 mmol) in 3 mL dichloromethane was added $MeSSiMe_3$ (0.3 mL, 2.3 mmol). After stirring for 12 h at room temperature, 20 mL anhydrous hexane was added to the reaction mixture and stored at -20 ^oC. The solution was filtered off and the

resulting dark brown solid was crystallized with $CHCl_3$/hexane to give single crystals (< 5%).

$[RuCl_2(DMSO)_4]$[34] **72.** To a suspension of trichlororuthenium chloride (III) hydrate (200 mg, 0.22 mmol) was added an excess of dimethylsulfoxide. The solution was kept at 80 ^oC for 8 h. The resulting solution was evaporated at reduced pressure in a vacuum desiccator. Crystals were obtained after recrystallization from dimethyl sulfoxide (86 %).

$[RuCl_3(CH_3CN)_3]$ 73. To a suspension of trichlororuthenium chloride (III) hydrate (200 mg, 0.22 mmol) was added an excess of acetonitrile. The solution was kept at 70 ^oC for 8 h. The resulting solution was evaporated at reduced pressure in a vacuum desiccator. Crystals were obtained after recrystallization from acetonitrile (78%).

3. 3.2. Propargylic Substitution Reactions



55 **71**

[4-(Naphthalen-2-yl)-5-yn-2-one] 71. A flame-dried flask (25 mL) equipped with a Teflon stirbar was charged with 1-(naphthalene-2-yl)prop-2-yn-1-ol **55** (25 mg, 0.13 mmol) and NH_4BF_4 (3 mg, 0.026 mmol) in 5 ml of acetone. Catalyst **68** (11 mg, 0.026

mmol) was then added at room temperature. After stirring for 12 h, brine was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate three times and the combined organic layers were dried over Na_2SO_4. After filtration and concentration, the mixture was purified by flash column chromatography (20 % ethyl acetate in hexane) to yield 4-(naphthalene-2-yl)hex-5-yn-2-one (<5 mg, <10 % yield; R_f 0.45 (20 % ethylacetate in hexane). ^{1}H NMR δ 2,14 (s, 3H), 2.32 (s,1H), 2.90 (dd, 1H, J = 17 and 5.9 Hz), 3.07 (dd, 1H, J = 17 and 8.1 Hz), 4.37 (t, 1H, J = 7.1 Hz), 7.44-7.49 (m, 3H), 7.82 (t, 4H, J = 8.3 Hz).

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3.5 X-Ray Crystal Structure Analysis

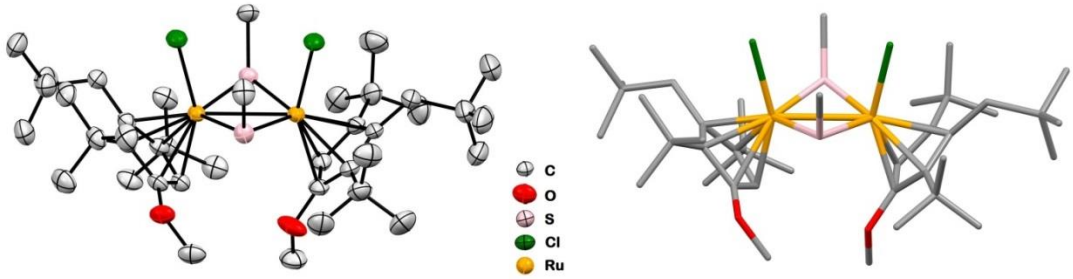


Table 3.5.1. Crystal Data and Structure Refinement for **69**.

Identification code: Compound **69**

Empirical formula: $C_{42}\ H_{74}\ C_{l8}\ O_2\ Ru_2\ S_2$

Formula weight: 1160.87

Temperature: 223(2) K

Wavelength: 0.71073 A

Crystal system, space group: Orthorhombic, P2(1)2(1)2(1)

Unit cell dimensions: a = 15.1435(12) A alpha = 90 deg.
b = 18.0477(14) A beta = 90 deg.
c = 19.1243(14) A gamma = 90 deg.

Volume: 5226.8(7) A^3

Z, Calculated density: 4, 1.475 Mg/m^3

Absorption coefficient: 1.099 mm^-1

F(000): 2392

Crystal color and shape: Dark magenta trigonal column

Crystal size: 0.40 x 0.35 x 0.30 mm

Theta range for data collection: 1.76 to 25.05 deg.

Limiting indices: -17<=h<=18, 0<=k<=21, 0<=l<=22

Reflections collected / unique: 26846 / 9238 [R(int) = 0.0279]

Completeness to theta = 25.05, 99.7 %

Absorption correction: Empirical

Max. and min. transmission: 0.9910 and 0.8202

Refinement method: Full-matrix least-squares on F^2

Data / restraints / parameters: 8779 / 0 / 479

Goodness-of-fit on F^2: 1.024

Final R indices [I>4sigma(I)]: R1 = 0.0361, wR2 = 0.0868

R indices (all data): R1 = 0.0377, wR2 = 0.0885

Absolute structure parameter: -0.02(3)

Largest diff. peak and hole: 1.021 and -1.042 e.A^-3

Table 3.5.2. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (A^2 x 10^3) for **69**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ru(1)	3976(1)	3702(1)	3007(1)	25(1)
Ru(2)	5400(1)	4101(1)	2095(1)	27(1)
Cl(1)	3359(1)	4892(1)	3351(1)	36(1)
Cl(2)	5367(1)	5440(1)	2129(1)	38(1)
S(1)	3909(1)	4049(1)	1844(1)	30(1)
S(2)	5386(1)	4065(1)	3311(1)	34(1)
O(1)	4824(2)	2523(2)	4166(2)	39(1)
O(2)	6272(3)	2507(2)	2406(2)	56(1)
C(1)	3376(3)	4934(3)	1691(3)	42(1)
C(2)	5464(4)	4970(3)	3718(3)	44(1)
C(3)	2784(3)	3093(2)	3349(2)	32(1)
C(4)	3198(3)	2666(2)	2798(2)	30(1)
C(5)	4065(3)	2460(2)	3018(2)	31(1)
C(6)	4161(3)	2688(2)	3728(2)	31(1)
C(7)	3421(3)	3127(2)	3936(2)	30(1)
C(8)	1874(3)	3452(3)	3347(3)	36(1)
C(9)	1033(4)	3020(3)	3614(3)	52(1)
C(10)	422(4)	3586(4)	3972(4)	71(2)
C(11)	486(4)	2693(4)	3010(4)	66(2)
C(12)	1257(4)	2387(3)	4118(3)	58(2)
C(13)	2817(3)	2316(2)	2125(3)	35(1)
C(14)	2139(4)	2793(3)	1737(3)	45(1)
C(15)	3547(4)	2125(3)	1600(3)	44(1)
C(16)	2402(4)	1571(3)	2368(3)	46(1)
C(17)	5509(4)	2037(3)	3914(3)	46(1)
C(18)	3352(4)	3399(3)	4707(3)	41(1)
C(19)	2552(4)	3893(3)	4868(3)	48(1)
C(20)	3309(5)	2709(3)	5181(3)	53(2)

Table 3.5.2. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (A^2 x 10^3) for **69**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)	
C(30)	8669(4)	5240(4)	1076(4)	75(2)	
C(31)	8150(4)	4178(4)	333(4)	61(2)	
C(32)	5432(4)	4019(3)	307(3)	48(1)	
C(33)	5115(5)	4823(4)	254(3)	65(2)	
C(34)	6075(5)	3852(4)	-294(3)	69(2)	
C(35)	4632(4)	3513(4)	198(3)	58(2)	
C(36)	6236(4)	1798(3)	2088(4)	56(2)	
C(37)	7614(4)	3806(3)	2506(3)	48(1)	
C(38)	7761(4)	4605(3)	2754(4)	60(2)	
C(39)	7519(4)	3336(4)	3174(3)	58(2)	
C(40)	8437(4)	3500(4)	2132(4)	69(2)	
C(41)	1417(3)	5553(4)	2636(4)	55(2)	
Cl(3)	1670(11)	6276(6)	2067(5)	92(1)	
Cl(4)	978(5)	5892(4)	3413(3)	92(1)	
Cl(5)	688(4)	4937(3)	2241(3)	92(1)	
C(42)	6733(2)	1280(2)	284(2)	53(2)	
Cl(6)	5649(2)	1480(3)	48(3)	83(1)	
Cl(7)	7248(3)	751(2)	-358(2)	83(1)	
Cl(8)	7317(3)	2094(2)	436(3)	83(1)	
C(41')	1298(3)	5717(3)	2652(2)	55(2)	
Cl(3')	1543(5)	6208(4)	1893(3)	92(1)	
Cl(4')	1129(4)	6319(3)	3351(2)	92(1)	
Cl(5')	377(4)	5158(3)	2523(3)	92(1)	
C(42')	6263(3)	937(2)	41(2)	53(2)	
Cl(6')	5449(3)	1579(4)	256(4)	82(1)	
Cl(7')	6096(4)	590(3)	-797(3)	82(1)	
Cl(8')	7305(3)	1336(3)	113(3)	82(1)	
C(41'')	1259(4)	5490(5)	2542(4)	55(2)	
Cl(3'')	1554(13)	6296(6)	2100(6)	90(1)	
Cl(4'')	457(5)	5675(4)	3170(3)	90(1)	

Cl(5")	889(5)	4822(4)	1955(4)	90(1)
C(42")	6484(5)	1130(4)	221(3)	53(2)
Cl(6")	5388(5)	1403(6)	317(6)	81(2)
Cl(7")	6636(6)	669(5)	-569(5)	81(2)
Cl(8")	7181(6)	1894(5)	278(6)	81(2)

Table 3.5.3. Bond lengths [A] and angles [deg] for **69**.

Ru(1)-C(3)	2.212(5)
Ru(1)-C(7)	2.222(4)
Ru(1)-C(4)	2.245(4)
Ru(1)-C(5)	2.244(4)
Ru(1)-C(6)	2.308(4)
Ru(1)-S(2)	2.3074(12)
Ru(1)-S(1)	2.3129(11)
Ru(1)-Cl(1)	2.4334(12)
Ru(1)-Ru(2)	2.8657(5)
Ru(2)-C(24)	2.178(5)
Ru(2)-C(25)	2.220(4)
Ru(2)-C(23)	2.240(5)
Ru(2)-C(26)	2.275(4)
Ru(2)-C(22)	2.295(5)
Ru(2)-S(1)	2.3107(12)
Ru(2)-S(2)	2.3257(12)
Ru(2)-Cl(2)	2.4184(11)
S(1)-C(1)	1.812(5)
S(2)-C(2)	1.813(5)
O(1)-C(6)	1.341(5)
O(1)-C(17)	1.441(6)
O(2)-C(25)	1.367(6)
O(2)-C(36)	1.418(6)
C(3)-C(4)	1.448(6)
C(3)-C(7)	1.482(7)
C(3)-C(8)	1.524(7)
C(4)-C(5)	1.427(6)

Table 3.5.3. Bond lengths [A] and angles [deg] for **69**.

C(7)-C(18)	1.557(6)
C(8)-C(9)	1.578(7)
C(9)-C(12)	1.531(8)
C(9)-C(11)	1.540(9)
C(9)-C(10)	1.539(8)
C(13)-C(14)	1.532(7)
C(13)-C(15)	1.532(7)
C(13)-C(16)	1.555(7)
C(18)-C(21)	1.534(8)
C(18)-C(19)	1.536(8)
C(18)-C(20)	1.542(7)
C(22)-C(26)	1.456(7)
C(22)-C(23)	1.460(7)
C(22)-C(27)	1.522(7)
C(23)-C(24)	1.430(7)
C(23)-C(32)	1.554(7)
C(24)-C(25)	1.391(7)
C(25)-C(26)	1.438(7)
C(26)-C(37)	1.541(7)
C(27)-C(28)	1.596(7)
C(28)-C(30)	1.526(10)
C(28)-C(29)	1.538(9)
C(28)-C(31)	1.554(8)
C(32)-C(35)	1.531(9)
C(32)-C(33)	1.531(8)
C(32)-C(34)	1.537(7)
C(37)-C(38)	1.534(8)
C(37)-C(39)	1.540(8)
C(37)-C(40)	1.539(8)
C(41)-Cl(4)	1.7400
C(41)-Cl(5)	1.7400
C(41)-Cl(3)	1.7400
C(42)-Cl(7)	1.7399
C(42)-Cl(8)	1.7399
C(42)-Cl(6)	1.7400
C(41')-Cl(5')	1.7399

Table 3.5.3. Bond lengths [A] and angles [deg] for **69**.

C(42')-Cl(7')	1.7399
C(42')-Cl(8')	1.7400
C(41")-Cl(5")	1.7400
C(41")-Cl(4")	1.7401
C(41")-Cl(3")	1.7401
C(42")-Cl(7")	1.7399
C(42")-Cl(8")	1.7400
C(42")-Cl(6")	1.7401
C(3)-Ru(1)-C(7)	39.05(17)
C(3)-Ru(1)-C(4)	37.92(17)
C(7)-Ru(1)-C(4)	63.62(16)
C(3)-Ru(1)-C(5)	63.28(17)
C(7)-Ru(1)-C(5)	63.23(17)
C(4)-Ru(1)-C(5)	37.05(16)
C(3)-Ru(1)-C(6)	61.87(17)
C(7)-Ru(1)-C(6)	36.70(17)
C(4)-Ru(1)-C(6)	60.64(16)
C(5)-Ru(1)-C(6)	36.48(16)
C(3)-Ru(1)-S(2)	145.28(13)
C(7)-Ru(1)-S(2)	106.34(13)
C(4)-Ru(1)-S(2)	140.05(12)
C(5)-Ru(1)-S(2)	103.06(12)
C(6)-Ru(1)-S(2)	87.89(12)
C(3)-Ru(1)-S(1)	112.50(13)
C(7)-Ru(1)-S(1)	151.47(13)
C(4)-Ru(1)-S(1)	91.78(12)
C(5)-Ru(1)-S(1)	106.36(12)
C(6)-Ru(1)-S(1)	142.60(12)
S(2)-Ru(1)-S(1)	101.86(4)
C(3)-Ru(1)-Cl(1)	92.59(12)
C(7)-Ru(1)-Cl(1)	92.90(12)
C(4)-Ru(1)-Cl(1)	125.58(12)
C(5)-Ru(1)-Cl(1)	154.40(12)
C(6)-Ru(1)-Cl(1)	125.81(12)
S(2)-Ru(1)-Cl(1)	92.09(4)

Table 3.5.3. Bond lengths [A] and angles [deg] for **69**.

C(4)-Ru(1)-Ru(2)	119.69(12)
C(5)-Ru(1)-Ru(2)	102.19(12)
C(6)-Ru(1)-Ru(2)	118.14(12)
S(2)-Ru(1)-Ru(2)	52.08(3)
S(1)-Ru(1)-Ru(2)	51.66(3)
Cl(1)-Ru(1)-Ru(2)	103.40(3)
C(24)-Ru(2)-C(25)	36.86(19)
C(24)-Ru(2)-C(23)	37.75(17)
C(25)-Ru(2)-C(23)	62.19(18)
C(24)-Ru(2)-C(26)	62.93(19)
C(25)-Ru(2)-C(26)	37.30(17)
C(23)-Ru(2)-C(26)	63.44(18)
C(24)-Ru(2)-C(22)	62.03(19)
C(25)-Ru(2)-C(22)	61.08(17)
C(23)-Ru(2)-C(22)	37.55(19)
C(26)-Ru(2)-C(22)	37.15(17)
C(24)-Ru(2)-S(1)	91.44(14)
C(25)-Ru(2)-S(1)	120.39(13)
C(23)-Ru(2)-S(1)	96.64(14)
C(26)-Ru(2)-S(1)	154.38(13)
C(22)-Ru(2)-S(1)	131.66(13)
C(24)-Ru(2)-S(2)	126.10(14)
C(25)-Ru(2)-S(2)	95.40(14)
C(23)-Ru(2)-S(2)	156.49(13)
C(26)-Ru(2)-S(2)	94.70(13)
C(22)-Ru(2)-S(2)	126.96(13)
S(1)-Ru(2)-S(2)	101.38(4)
C(24)-Ru(2)-Cl(2)	142.24(14)
C(25)-Ru(2)-Cl(2)	145.63(13)
C(23)-Ru(2)-Cl(2)	104.57(13)
C(26)-Ru(2)-Cl(2)	108.50(12)
C(22)-Ru(2)-Cl(2)	88.75(12)
S(1)-Ru(2)-Cl(2)	91.45(4)
S(2)-Ru(2)-Cl(2)	90.04(4)
C(24)-Ru(2)-Ru(1)	108.53(13)
C(25)-Ru(2)-Ru(1)	107.25(13)

Table 3.5.3. Bond lengths [A] and angles [deg] for **69**.

S(1)-Ru(2)-Ru(1)	51.73(3)
S(2)-Ru(2)-Ru(1)	51.50(3)
Cl(2)-Ru(2)-Ru(1)	102.64(3)
C(1)-S(1)-Ru(2)	115.67(19)
C(1)-S(1)-Ru(1)	114.44(18)
Ru(2)-S(1)-Ru(1)	76.60(3)
C(2)-S(2)-Ru(1)	115.08(19)
C(2)-S(2)-Ru(2)	113.81(18)
Ru(1)-S(2)-Ru(2)	76.42(4)
C(6)-O(1)-C(17)	117.8(4)
C(25)-O(2)-C(36)	116.4(4)
C(4)-C(3)-C(7)	106.9(4)
C(4)-C(3)-C(8)	128.1(4)
C(7)-C(3)-C(8)	125.0(4)
C(4)-C(3)-Ru(1)	72.3(3)
C(7)-C(3)-Ru(1)	70.9(3)
C(8)-C(3)-Ru(1)	121.8(3)
C(5)-C(4)-C(3)	108.8(4)
C(5)-C(4)-C(13)	118.8(4)
C(3)-C(4)-C(13)	131.4(4)
C(5)-C(4)-Ru(1)	71.4(2)
C(3)-C(4)-Ru(1)	69.8(2)
C(13)-C(4)-Ru(1)	133.2(3)
C(6)-C(5)-C(4)	107.4(4)
C(6)-C(5)-Ru(1)	74.2(2)
C(4)-C(5)-Ru(1)	71.5(2)
O(1)-C(6)-C(5)	127.4(4)
O(1)-C(6)-C(7)	122.4(4)
C(5)-C(6)-C(7)	110.2(4)
O(1)-C(6)-Ru(1)	129.7(3)
C(5)-C(6)-Ru(1)	69.3(2)
C(7)-C(6)-Ru(1)	68.4(2)
C(6)-C(7)-C(3)	106.0(4)
C(6)-C(7)-C(18)	119.5(4)
C(3)-C(7)-C(18)	133.3(4)
C(6)-C(7)-Ru(1)	74.9(3)

Table 3.5.3. Bond lengths [A] and angles [deg] for **69**.

C(12)-C(9)-C(11)	107.8(5)
C(12)-C(9)-C(10)	110.4(5)
C(11)-C(9)-C(10)	105.4(5)
C(12)-C(9)-C(8)	113.2(5)
C(11)-C(9)-C(8)	112.3(5)
C(10)-C(9)-C(8)	107.6(5)
C(14)-C(13)-C(15)	107.1(4)
C(14)-C(13)-C(4)	115.1(4)
C(15)-C(13)-C(4)	111.6(4)
C(14)-C(13)-C(16)	111.0(4)
C(15)-C(13)-C(16)	107.0(4)
C(4)-C(13)-C(16)	104.8(4)
C(21)-C(18)-C(19)	106.0(4)
C(21)-C(18)-C(20)	109.0(5)
C(19)-C(18)-C(20)	108.6(5)
C(21)-C(18)-C(7)	110.2(4)
C(19)-C(18)-C(7)	115.3(4)
C(20)-C(18)-C(7)	107.7(4)
C(26)-C(22)-C(23)	109.0(4)
C(26)-C(22)-C(27)	127.7(5)
C(23)-C(22)-C(27)	123.2(4)
C(26)-C(22)-Ru(2)	70.7(2)
C(23)-C(22)-Ru(2)	69.2(3)
C(27)-C(22)-Ru(2)	123.2(3)
C(24)-C(23)-C(22)	105.9(4)
C(24)-C(23)-C(32)	122.5(5)
C(22)-C(23)-C(32)	131.2(5)
C(24)-C(23)-Ru(2)	68.8(3)
C(22)-C(23)-Ru(2)	73.3(3)
C(32)-C(23)-Ru(2)	127.9(3)
C(25)-C(24)-C(23)	109.4(4)
C(25)-C(24)-Ru(2)	73.2(3)
C(23)-C(24)-Ru(2)	73.5(3)
O(2)-C(25)-C(24)	124.5(5)
O(2)-C(25)-C(26)	124.8(5)
C(24)-C(25)-C(26)	110.6(4)

Table 3.5.3. Bond lengths [A] and angles [deg] for **69**.

C(25)-C(26)-C(22)	104.9(4)
C(25)-C(26)-C(37)	125.1(4)
C(22)-C(26)-C(37)	129.0(4)
C(25)-C(26)-Ru(2)	69.3(2)
C(22)-C(26)-Ru(2)	72.2(3)
C(37)-C(26)-Ru(2)	130.9(3)
C(22)-C(27)-C(28)	122.1(4)
C(30)-C(28)-C(29)	106.7(6)
C(30)-C(28)-C(31)	109.3(5)
C(29)-C(28)-C(31)	109.1(6)
C(30)-C(28)-C(27)	109.9(5)
C(29)-C(28)-C(27)	106.6(5)
C(31)-C(28)-C(27)	114.8(5)
C(35)-C(32)-C(33)	107.9(5)
C(35)-C(32)-C(34)	106.4(5)
C(33)-C(32)-C(34)	109.6(5)
C(35)-C(32)-C(23)	109.2(4)
C(33)-C(32)-C(23)	113.9(5)
C(34)-C(32)-C(23)	109.6(5)
C(38)-C(37)-C(39)	106.0(5)
C(38)-C(37)-C(26)	113.0(4)
C(39)-C(37)-C(26)	113.7(5)
C(38)-C(37)-C(40)	111.3(5)
C(39)-C(37)-C(40)	105.3(5)
C(26)-C(37)-C(40)	107.3(5)
Cl(4)-C(41)-Cl(5)	110.7
Cl(4)-C(41)-Cl(3)	110.7
Cl(5)-C(41)-Cl(3)	110.4
Cl(7)-C(42)-Cl(8)	110.7
Cl(7)-C(42)-Cl(6)	110.7
Cl(8)-C(42)-Cl(6)	110.4
Cl(5')-C(41')-Cl(3')	110.4
Cl(5')-C(41')-Cl(4')	110.7
Cl(3')-C(41')-Cl(4')	110.7
Cl(6')-C(42')-Cl(7')	110.7
Cl(6')-C(42')-Cl(8')	110.4

Table 3.5.3. Bond lengths [A] and angles [deg] for **69**.

Cl(4")-C(41")-Cl(3")	110.7
Cl(7")-C(42")-Cl(8")	110.7
Cl(7")-C(42")-Cl(6")	110.7
Cl(8")-C(42")-Cl(6")	110.4

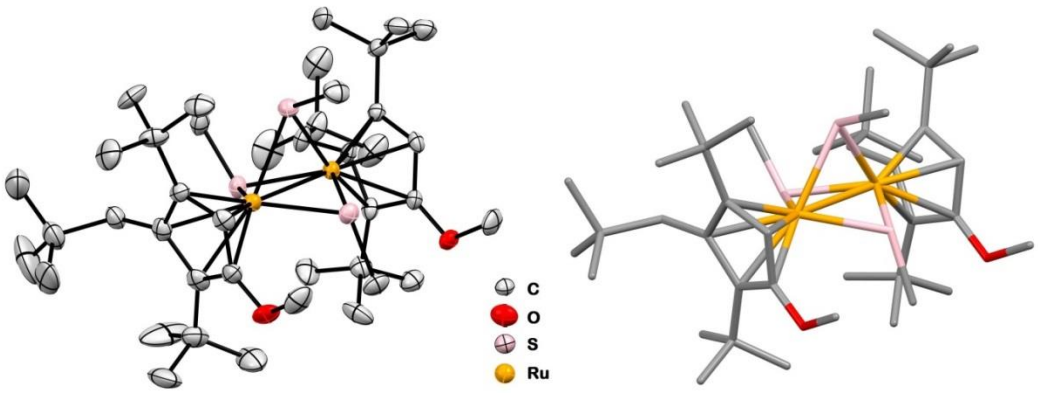


Table 3.5.4. Crystal data and structure refinement for **70**.

Identification code: Compound **70**

Empirical formula: C_{42} H_{77} Cl_3 O2 Ru_2 S_3

Formula weight: 1018.71

Temperature: 223(2) K

Wavelength: 0.71073 A

Crystal system, space group: Orthorhombic, Pca2(1)

Unit cell dimensions: a = 23.7497(19) A alpha = 90 deg.
b = 12.4123(10) A beta = 90 deg.
c = 32.5828(26) A gamma = 90 deg.

Volume: 9605.0(13) A^3

Z, Calculated density: 8, 1.409 Mg/m^3

Absorption coefficient: 0.958 mm^-1

F(000): 4256

Crystal color and shape: Dark red column

Crystal size: 0.30 x 0.15 x 0.12 mm

Theta range for data collection: 1.64 to 25.04 deg.

Limiting indices: 0<=h<=28, 0<=k<=14, -38<=l<=38

Reflections collected / unique: 49199 / 18206 [R(int) = 0.0392]

Completeness to theta = 25.04, 100.0 %

Absorption correction: Empirical

Max. and min. transmission: 0.9921 and 0.7839

Refinement method: Full-matrix least-squares on F^2

Data / restraints / parameters: 12330 / 1 / 924

Goodness-of-fit on F^2: 0.940

Final R indices [I>4sigma(I)]: R1 = 0.0282, wR2 = 0.0683

R indices (all data): R1 = 0.0420, wR2 = 0.0747

Absolute structure parameter: 0.46(2)

Largest diff. peak and hole: 0.881 and -0.590 e.A^-3

Table 3.5.5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **70**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ru(1)	7733(1)	1999(1)	4909(1)	19(1)
Ru(2)	7045(1)	3404(1)	4504(1)	20(1)
Ru(3)	4403(1)	8389(1)	1755(1)	20(1)
Ru(4)	5094(1)	6995(1)	1352(1)	19(1)
Cl(1)	7281(1)	9750(1)	1436(1)	45(1)
Cl(2)	9945(1)	4700(1)	4853(1)	38(1)
S(1)	7443(1)	3735(1)	5179(1)	24(1)
S(2)	6749(1)	1923(1)	4895(1)	25(1)
S(3)	7986(1)	3092(1)	4366(1)	25(1)
S(4)	4794(1)	8718(1)	1077(1)	23(1)
S(5)	4109(1)	6903(1)	1367(1)	25(1)
S(6)	5346(1)	8116(1)	1884(1)	24(1)
O(1)	7442(1)	-590(3)	5017(1)	26(1)
O(2)	5831(1)	2676(3)	4088(1)	34(1)
O(3)	3207(2)	7641(3)	2192(1)	40(1)
O(4)	4827(1)	4391(2)	1279(1)	30(1)
C(1)	6912(2)	3587(4)	5579(2)	37(1)
C(2)	6440(2)	798(4)	4617(2)	34(1)

Table 3.5.5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **70**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(13)	9686(2)	34(4)	4843(2)	50(2)
C(14)	8654(2)	2116(4)	5706(2)	26(1)
C(15)	8983(2)	3133(4)	5595(2)	37(1)
C(16)	8197(2)	2433(4)	6010(2)	38(1)
C(17)	9037(2)	1309(4)	5933(2)	42(2)
C(18)	7100(2)	-784(4)	5371(2)	38(1)
C(19)	8232(2)	-145(4)	4328(2)	29(1)
C(20)	8615(3)	361(5)	4003(2)	44(2)
C(21)	8432(2)	-1302(4)	4417(2)	33(1)
C(22)	7642(2)	-231(5)	4135(2)	43(2)
C(23)	6973(2)	4571(4)	3972(2)	28(1)
C(24)	6690(2)	4989(4)	4334(2)	25(1)
C(25)	6241(2)	4266(4)	4427(2)	27(1)
C(26)	6225(2)	3446(4)	4126(2)	29(1)
C(27)	6695(2)	3544(4)	3857(2)	29(1)
C(28)	7480(2)	5079(4)	3758(2)	30(1)
C(29)	7395(3)	5916(5)	3403(2)	48(2)
C(30)	7823(4)	5676(8)	3063(2)	104(3)
C(31)	7536(3)	7060(5)	3548(2)	69(2)
C(32)	6801(3)	5932(6)	3221(2)	71(2)
C(33)	6737(2)	6087(4)	4565(2)	33(1)
C(34)	7337(2)	6496(4)	4616(2)	41(2)
C(35)	6480(2)	5965(4)	5003(2)	41(2)
C(36)	6357(3)	6892(4)	4339(2)	51(2)
C(37)	5391(2)	2687(4)	4391(2)	44(2)
C(38)	6754(2)	2808(5)	3472(2)	39(1)
C(39)	7317(3)	2895(6)	3254(2)	89(3)
C(40)	6293(3)	3122(5)	3173(2)	66(2)

Table 3.5.5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **70**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(51)	4710(3)	10920(5)	2860(2)	45(2)
C(52)	5040(4)	10565(8)	3243(2)	106(3)
C(53)	4925(3)	12022(5)	2747(2)	80(3)
C(54)	4087(3)	11041(5)	2963(2)	66(2)
C(55)	4083(2)	11043(4)	1692(2)	29(1)
C(56)	4682(2)	11466(4)	1637(2)	41(2)
C(57)	3828(2)	10926(4)	1273(2)	43(2)
C(58)	3729(3)	11880(5)	1922(2)	56(2)
C(59)	2748(2)	7669(5)	1901(2)	54(2)
C(60)	4186(3)	7774(4)	2782(2)	38(1)
C(61)	4808(3)	7722(7)	2921(2)	84(3)
C(62)	3825(3)	8146(5)	3149(2)	72(2)
C(63)	3995(3)	6606(5)	2692(2)	67(2)
C(64)	5970(2)	6301(3)	1340(2)	22(1)
C(65)	5767(2)	6487(4)	929(2)	23(1)
C(66)	5283(2)	5825(4)	869(2)	22(1)
C(67)	5211(2)	5205(4)	1230(2)	21(1)
C(68)	5592(2)	5514(4)	1542(2)	25(1)
C(69)	6488(2)	6834(4)	1529(2)	25(1)
C(70)	7085(2)	6254(4)	1496(2)	32(1)
C(71)	7392(2)	6454(6)	1903(2)	56(2)
C(72)	7451(2)	6774(5)	1160(2)	48(2)
C(73)	7047(2)	5065(4)	1410(2)	48(2)
C(74)	6006(2)	7087(4)	555(2)	25(1)
C(75)	6315(2)	8147(4)	663(2)	33(1)
C(76)	5532(2)	7391(4)	256(2)	31(1)
C(77)	6392(2)	6297(4)	322(2)	35(1)
C(78)	4467(2)	4184(4)	923(2)	33(1)

Table 3.5.5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **70**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(84)	7010(3)	9663(8)	2466(3)	65(3)
Cl(5)	7642(2)	9692(4)	2741(2)	89(1)
Cl(6)	6533(2)	8715(4)	2659(1)	89(1)
C(84')	7126(4)	9007(13)	2544(5)	65(3)
Cl(5')	7595(3)	9982(7)	2727(4)	89(1)
Cl(6')	6480(3)	9024(6)	2803(2)	89(1)
C(84'')	6706(12)	10909(14)	2542(5)	65(3)
Cl(5'')	6462(5)	11385(7)	2069(3)	89(1)
Cl(6'')	6433(5)	9640(8)	2666(3)	93

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

Ru(1)-C(6)	2.208(4)
Ru(1)-C(5)	2.213(5)
Ru(1)-C(4)	2.252(4)
Ru(1)-C(8)	2.270(4)
Ru(1)-C(7)	2.298(5)
Ru(1)-S(3)	2.3083(12)
Ru(1)-S(2)	2.3393(12)
Ru(1)-S(1)	2.4264(12)
Ru(1)-Ru(2)	2.7299(6)
Ru(2)-C(25)	2.204(5)
Ru(2)-C(24)	2.211(4)

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

Ru(2)-S(3)	2.3114(13)
Ru(2)-S(2)	2.3430(13)
Ru(2)-S(1)	2.4275(13)
Ru(3)-C(47)	2.193(5)
Ru(3)-C(46)	2.217(5)
Ru(3)-C(45)	2.250(5)
Ru(3)-C(49)	2.281(5)
Ru(3)-C(48)	2.298(5)
Ru(3)-S(6)	2.3046(13)
Ru(3)-S(5)	2.3416(13)
Ru(3)-S(4)	2.4301(13)
Ru(3)-Ru(4)	2.7228(6)
Ru(4)-C(66)	2.186(5)
Ru(4)-C(65)	2.201(5)
Ru(4)-C(64)	2.251(4)
Ru(4)-C(68)	2.272(5)
Ru(4)-C(67)	2.274(5)
Ru(4)-S(6)	2.3034(12)
Ru(4)-S(5)	2.3424(12)
Ru(4)-S(4)	2.4264(12)
S(1)-C(1)	1.825(5)
S(2)-C(2)	1.819(5)
S(3)-C(3)	1.813(5)
S(4)-C(42)	1.833(5)
S(5)-C(43)	1.816(5)
S(6)-C(44)	1.818(5)
O(1)-C(7)	1.338(5)
O(1)-C(18)	1.431(6)
O(2)-C(26)	1.343(6)
O(2)-C(37)	1.439(6)
O(3)-C(48)	1.342(6)
O(3)-C(59)	1.447(6)
O(4)-C(67)	1.371(5)
O(4)-C(78)	1.464(6)
C(4)-C(5)	1.428(7)
C(4)-C(8)	1.480(6)

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

C(6)-C(7)	1.418(6)
C(7)-C(8)	1.424(6)
C(8)-C(19)	1.547(7)
C(9)-C(10)	1.580(7)
C(10)-C(13)	1.527(7)
C(10)-C(11)	1.536(8)
C(10)-C(12)	1.541(8)
C(14)-C(16)	1.523(7)
C(14)-C(15)	1.527(7)
C(14)-C(17)	1.540(7)
C(19)-C(20)	1.530(7)
C(19)-C(22)	1.539(7)
C(19)-C(21)	1.541(7)
C(23)-C(24)	1.451(7)
C(23)-C(27)	1.483(7)
C(23)-C(28)	1.529(7)
C(24)-C(25)	1.428(7)
C(24)-C(33)	1.561(7)
C(25)-C(26)	1.413(7)
C(26)-C(27)	1.424(7)
C(27)-C(38)	1.560(7)
C(28)-C(29)	1.569(7)
C(29)-C(31)	1.534(8)
C(29)-C(32)	1.530(8)
C(29)-C(30)	1.531(9)
C(33)-C(34)	1.522(7)
C(33)-C(36)	1.534(7)
C(33)-C(35)	1.561(8)
C(38)-C(41)	1.491(8)
C(38)-C(40)	1.516(8)
C(38)-C(39)	1.516(9)
C(45)-C(46)	1.443(7)
C(45)-C(49)	1.481(7)
C(45)-C(50)	1.504(7)
C(46)-C(47)	1.442(6)
C(46)-C(55)	1.551(7)

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

C(50)-C(51)	1.601(7)
C(51)-C(53)	1.506(8)
C(51)-C(54)	1.526(9)
C(51)-C(52)	1.538(10)
C(55)-C(57)	1.500(7)
C(55)-C(56)	1.528(7)
C(55)-C(58)	1.532(7)
C(60)-C(61)	1.546(9)
C(60)-C(62)	1.542(7)
C(60)-C(63)	1.547(8)
C(64)-C(65)	1.441(7)
C(64)-C(68)	1.481(6)
C(64)-C(69)	1.528(6)
C(65)-C(66)	1.426(6)
C(65)-C(74)	1.536(7)
C(66)-C(67)	1.417(7)
C(67)-C(68)	1.412(7)
C(68)-C(79)	1.548(7)
C(69)-C(70)	1.592(7)
C(70)-C(73)	1.505(7)
C(70)-C(71)	1.536(8)
C(70)-C(72)	1.541(8)
C(74)-C(76)	1.536(7)
C(74)-C(77)	1.545(7)
C(74)-C(75)	1.546(6)
C(79)-C(80)	1.530(7)
C(79)-C(81)	1.546(7)
C(79)-C(82)	1.541(7)
C(83)-Cl(4)	1.7498
C(83)-Cl(3)	1.7499
C(83')-Cl(4')	1.7497
C(83')-Cl(3')	1.7499
C(84)-Cl(6)	1.7500
C(84)-Cl(5)	1.7501
C(84')-Cl(6')	1.7498
C(84')-Cl(5')	1.7499

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

C(6)-Ru(1)-C(5)	37.70(17)
C(6)-Ru(1)-C(4)	62.20(17)
C(5)-Ru(1)-C(4)	37.28(17)
C(6)-Ru(1)-C(8)	62.69(17)
C(5)-Ru(1)-C(8)	63.54(17)
C(4)-Ru(1)-C(8)	38.20(16)
C(6)-Ru(1)-C(7)	36.63(16)
C(5)-Ru(1)-C(7)	61.51(17)
C(4)-Ru(1)-C(7)	60.88(16)
C(8)-Ru(1)-C(7)	36.33(16)
C(6)-Ru(1)-S(3)	153.26(13)
C(5)-Ru(1)-S(3)	117.68(12)
C(4)-Ru(1)-S(3)	91.38(12)
C(8)-Ru(1)-S(3)	99.70(12)
C(7)-Ru(1)-S(3)	134.75(13)
C(6)-Ru(1)-S(2)	100.69(13)
C(5)-Ru(1)-S(2)	136.20(13)
C(4)-Ru(1)-S(2)	153.87(12)
C(8)-Ru(1)-S(2)	117.58(13)
C(7)-Ru(1)-S(2)	93.43(12)
S(3)-Ru(1)-S(2)	105.52(5)
C(6)-Ru(1)-S(1)	111.65(13)
C(5)-Ru(1)-S(1)	103.40(12)
C(4)-Ru(1)-S(1)	127.31(12)
C(8)-Ru(1)-S(1)	165.39(13)
C(7)-Ru(1)-S(1)	144.94(12)
S(3)-Ru(1)-S(1)	80.16(4)
S(2)-Ru(1)-S(1)	76.11(4)
C(6)-Ru(1)-Ru(2)	152.64(13)
C(5)-Ru(1)-Ru(2)	156.92(12)
C(4)-Ru(1)-Ru(2)	145.15(12)
C(8)-Ru(1)-Ru(2)	135.35(12)
C(7)-Ru(1)-Ru(2)	141.06(12)
S(3)-Ru(1)-Ru(2)	53.83(3)
S(2)-Ru(1)-Ru(2)	54.40(3)
S(1)-Ru(1)-Ru(2)	55.79(3)

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

C(25)-Ru(2)-C(23)	62.38(19)
C(24)-Ru(2)-C(23)	37.80(18)
C(27)-Ru(2)-C(23)	38.15(18)
C(25)-Ru(2)-C(26)	36.43(18)
C(24)-Ru(2)-C(26)	61.53(17)
C(27)-Ru(2)-C(26)	36.24(18)
C(23)-Ru(2)-C(26)	60.81(18)
C(25)-Ru(2)-S(3)	153.73(14)
C(24)-Ru(2)-S(3)	117.92(13)
C(27)-Ru(2)-S(3)	100.71(13)
C(23)-Ru(2)-S(3)	91.80(13)
C(26)-Ru(2)-S(3)	135.75(14)
C(25)-Ru(2)-S(2)	100.56(14)
C(24)-Ru(2)-S(2)	136.09(14)
C(27)-Ru(2)-S(2)	117.01(13)
C(23)-Ru(2)-S(2)	153.42(13)
C(26)-Ru(2)-S(2)	93.16(13)
S(3)-Ru(2)-S(2)	105.30(4)
C(25)-Ru(2)-S(1)	111.05(14)
C(24)-Ru(2)-S(1)	103.02(13)
C(27)-Ru(2)-S(1)	165.73(13)
C(23)-Ru(2)-S(1)	127.86(14)
C(26)-Ru(2)-S(1)	144.03(14)
S(3)-Ru(2)-S(1)	80.08(4)
S(2)-Ru(2)-S(1)	76.02(4)
C(25)-Ru(2)-Ru(1)	152.18(14)
C(24)-Ru(2)-Ru(1)	156.61(12)
C(27)-Ru(2)-Ru(1)	135.75(13)
C(23)-Ru(2)-Ru(1)	145.43(13)
C(26)-Ru(2)-Ru(1)	141.17(13)
S(3)-Ru(2)-Ru(1)	53.72(3)
S(2)-Ru(2)-Ru(1)	54.27(3)
S(1)-Ru(2)-Ru(1)	55.76(3)
C(47)-Ru(3)-C(46)	38.18(17)
C(47)-Ru(3)-C(45)	62.77(18)
C(46)-Ru(3)-C(45)	37.68(18)

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

C(47)-Ru(3)-C(48)	36.66(18)
C(46)-Ru(3)-C(48)	61.70(18)
C(45)-Ru(3)-C(48)	60.82(17)
C(49)-Ru(3)-C(48)	36.18(18)
C(47)-Ru(3)-S(6)	153.15(13)
C(46)-Ru(3)-S(6)	116.95(13)
C(45)-Ru(3)-S(6)	90.80(13)
C(49)-Ru(3)-S(6)	99.80(15)
C(48)-Ru(3)-S(6)	134.87(14)
C(47)-Ru(3)-S(5)	100.58(13)
C(46)-Ru(3)-S(5)	136.55(13)
C(45)-Ru(3)-S(5)	153.89(12)
C(49)-Ru(3)-S(5)	117.42(13)
C(48)-Ru(3)-S(5)	93.61(13)
S(6)-Ru(3)-S(5)	105.83(4)
C(47)-Ru(3)-S(4)	112.00(14)
C(46)-Ru(3)-S(4)	103.71(14)
C(45)-Ru(3)-S(4)	127.88(13)
C(49)-Ru(3)-S(4)	165.94(12)
C(48)-Ru(3)-S(4)	145.36(14)
S(6)-Ru(3)-S(4)	79.60(4)
S(5)-Ru(3)-S(4)	75.87(4)
C(47)-Ru(3)-Ru(4)	152.81(13)
C(46)-Ru(3)-Ru(4)	157.02(13)
C(45)-Ru(3)-Ru(4)	144.41(13)
C(49)-Ru(3)-Ru(4)	134.65(13)
C(48)-Ru(3)-Ru(4)	140.91(13)
S(6)-Ru(3)-Ru(4)	53.76(3)
S(5)-Ru(3)-Ru(4)	54.47(3)
S(4)-Ru(3)-Ru(4)	55.84(3)
C(66)-Ru(4)-C(65)	37.92(17)
C(66)-Ru(4)-C(64)	62.87(18)
C(65)-Ru(4)-C(64)	37.75(17)
C(66)-Ru(4)-C(68)	63.41(18)
C(65)-Ru(4)-C(68)	64.00(18)
C(64)-Ru(4)-C(68)	38.24(16)

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

C(68)-Ru(4)-C(67)	36.19(17)
C(66)-Ru(4)-S(6)	152.78(13)
C(65)-Ru(4)-S(6)	117.07(13)
C(64)-Ru(4)-S(6)	90.21(13)
C(68)-Ru(4)-S(6)	98.52(13)
C(67)-Ru(4)-S(6)	133.59(13)
C(66)-Ru(4)-S(5)	100.86(13)
C(65)-Ru(4)-S(5)	136.42(13)
C(64)-Ru(4)-S(5)	154.73(12)
C(68)-Ru(4)-S(5)	118.32(13)
C(67)-Ru(4)-S(5)	94.52(12)
S(6)-Ru(4)-S(5)	105.84(5)
C(66)-Ru(4)-S(4)	112.37(13)
C(65)-Ru(4)-S(4)	103.61(13)
C(64)-Ru(4)-S(4)	127.07(12)
C(68)-Ru(4)-S(4)	165.30(13)
C(67)-Ru(4)-S(4)	146.47(13)
S(6)-Ru(4)-S(4)	79.70(4)
S(5)-Ru(4)-S(4)	75.93(4)
C(66)-Ru(4)-Ru(3)	153.21(13)
C(65)-Ru(4)-Ru(3)	157.10(12)
C(64)-Ru(4)-Ru(3)	143.92(12)
C(68)-Ru(4)-Ru(3)	134.11(13)
C(67)-Ru(4)-Ru(3)	141.14(12)
S(6)-Ru(4)-Ru(3)	53.80(3)
S(5)-Ru(4)-Ru(3)	54.44(3)
S(4)-Ru(4)-Ru(3)	55.96(3)
C(1)-S(1)-Ru(1)	111.44(18)
C(1)-S(1)-Ru(2)	111.15(18)
Ru(1)-S(1)-Ru(2)	68.45(3)
C(2)-S(2)-Ru(1)	116.44(17)
C(2)-S(2)-Ru(2)	116.94(18)
Ru(1)-S(2)-Ru(2)	71.33(4)
C(3)-S(3)-Ru(1)	111.51(18)
C(3)-S(3)-Ru(2)	111.49(18)
Ru(1)-S(3)-Ru(2)	72.45(4)

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

C(43)-S(5)-Ru(4)	117.10(17)
C(43)-S(5)-Ru(3)	116.58(18)
Ru(4)-S(5)-Ru(3)	71.08(4)
C(44)-S(6)-Ru(4)	111.46(17)
C(44)-S(6)-Ru(3)	111.67(16)
Ru(4)-S(6)-Ru(3)	72.44(4)
C(7)-O(1)-C(18)	116.0(4)
C(26)-O(2)-C(37)	115.7(4)
C(48)-O(3)-C(59)	116.1(4)
C(67)-O(4)-C(78)	115.2(4)
C(5)-C(4)-C(8)	108.6(4)
C(5)-C(4)-C(9)	125.6(4)
C(8)-C(4)-C(9)	125.8(4)
C(5)-C(4)-Ru(1)	69.9(3)
C(8)-C(4)-Ru(1)	71.6(2)
C(9)-C(4)-Ru(1)	123.2(3)
C(6)-C(5)-C(4)	107.5(4)
C(6)-C(5)-C(14)	118.1(4)
C(4)-C(5)-C(14)	133.7(4)
C(6)-C(5)-Ru(1)	71.0(3)
C(4)-C(5)-Ru(1)	72.8(3)
C(14)-C(5)-Ru(1)	128.3(3)
C(7)-C(6)-C(5)	108.3(4)
C(7)-C(6)-Ru(1)	75.1(3)
C(5)-C(6)-Ru(1)	71.3(3)
O(1)-C(7)-C(6)	125.9(4)
O(1)-C(7)-C(8)	123.9(4)
C(6)-C(7)-C(8)	110.1(4)
O(1)-C(7)-Ru(1)	128.8(3)
C(6)-C(7)-Ru(1)	68.3(3)
C(8)-C(7)-Ru(1)	70.8(3)
C(7)-C(8)-C(4)	105.1(4)
C(7)-C(8)-C(19)	121.0(4)
C(4)-C(8)-C(19)	132.9(4)
C(7)-C(8)-Ru(1)	72.9(3)
C(4)-C(8)-Ru(1)	70.2(2)

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

C(13)-C(10)-C(12)	107.4(5)
C(11)-C(10)-C(12)	105.3(5)
C(13)-C(10)-C(9)	112.8(4)
C(11)-C(10)-C(9)	106.9(4)
C(12)-C(10)-C(9)	111.8(5)
C(16)-C(14)-C(15)	107.8(4)
C(16)-C(14)-C(17)	106.1(4)
C(15)-C(14)-C(17)	110.4(5)
C(16)-C(14)-C(5)	111.2(4)
C(15)-C(14)-C(5)	115.3(4)
C(17)-C(14)-C(5)	105.6(4)
C(20)-C(19)-C(22)	106.6(5)
C(20)-C(19)-C(8)	114.1(4)
C(22)-C(19)-C(8)	111.2(4)
C(20)-C(19)-C(21)	109.2(4)
C(22)-C(19)-C(21)	107.0(4)
C(8)-C(19)-C(21)	108.4(4)
C(24)-C(23)-C(27)	107.9(4)
C(24)-C(23)-C(28)	126.0(5)
C(27)-C(23)-C(28)	126.2(5)
C(24)-C(23)-Ru(2)	69.1(3)
C(27)-C(23)-Ru(2)	71.2(3)
C(28)-C(23)-Ru(2)	123.6(3)
C(25)-C(24)-C(23)	107.1(4)
C(25)-C(24)-C(33)	119.9(5)
C(23)-C(24)-C(33)	132.1(4)
C(25)-C(24)-Ru(2)	70.9(3)
C(23)-C(24)-Ru(2)	73.1(3)
C(33)-C(24)-Ru(2)	128.9(3)
C(26)-C(25)-C(24)	109.0(5)
C(26)-C(25)-Ru(2)	75.7(3)
C(24)-C(25)-Ru(2)	71.4(3)
O(2)-C(26)-C(25)	126.5(5)
O(2)-C(26)-C(27)	123.3(5)
C(25)-C(26)-C(27)	110.1(5)
O(2)-C(26)-Ru(2)	128.4(3)

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

C(26)-C(27)-C(38)	121.0(4)
C(23)-C(27)-C(38)	131.8(5)
C(26)-C(27)-Ru(2)	73.2(3)
C(23)-C(27)-Ru(2)	70.7(3)
C(38)-C(27)-Ru(2)	132.0(3)
C(23)-C(28)-C(29)	120.5(4)
C(31)-C(29)-C(32)	108.0(6)
C(31)-C(29)-C(30)	105.0(6)
C(32)-C(29)-C(30)	109.6(6)
C(31)-C(29)-C(28)	110.9(5)
C(32)-C(29)-C(28)	114.4(5)
C(30)-C(29)-C(28)	108.6(5)
C(34)-C(33)-C(36)	112.7(5)
C(34)-C(33)-C(35)	107.3(5)
C(36)-C(33)-C(35)	105.8(4)
C(34)-C(33)-C(24)	114.2(4)
C(36)-C(33)-C(24)	107.2(4)
C(35)-C(33)-C(24)	109.3(4)
C(41)-C(38)-C(40)	108.4(5)
C(41)-C(38)-C(39)	106.4(6)
C(40)-C(38)-C(39)	108.6(6)
C(41)-C(38)-C(27)	111.3(5)
C(40)-C(38)-C(27)	107.5(5)
C(39)-C(38)-C(27)	114.5(5)
C(46)-C(45)-C(49)	108.9(4)
C(46)-C(45)-C(50)	125.1(4)
C(49)-C(45)-C(50)	126.0(5)
C(46)-C(45)-Ru(3)	69.9(3)
C(49)-C(45)-Ru(3)	72.1(3)
C(50)-C(45)-Ru(3)	126.0(3)
C(45)-C(46)-C(47)	106.7(4)
C(45)-C(46)-C(55)	133.6(4)
C(47)-C(46)-C(55)	119.4(5)
C(45)-C(46)-Ru(3)	72.4(3)
C(47)-C(46)-Ru(3)	70.0(3)
C(55)-C(46)-Ru(3)	127.1(3)

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

O(3)-C(48)-C(47)	125.2(5)
O(3)-C(48)-C(49)	124.0(5)
C(47)-C(48)-C(49)	110.8(4)
O(3)-C(48)-Ru(3)	128.9(3)
C(47)-C(48)-Ru(3)	67.6(3)
C(49)-C(48)-Ru(3)	71.3(3)
C(48)-C(49)-C(45)	104.9(4)
C(48)-C(49)-C(60)	123.1(5)
C(45)-C(49)-C(60)	131.2(5)
C(48)-C(49)-Ru(3)	72.5(3)
C(45)-C(49)-Ru(3)	69.8(3)
C(60)-C(49)-Ru(3)	129.3(3)
C(45)-C(50)-C(51)	119.3(4)
C(53)-C(51)-C(54)	107.0(6)
C(53)-C(51)-C(52)	106.6(6)
C(54)-C(51)-C(52)	110.0(6)
C(53)-C(51)-C(50)	110.2(5)
C(54)-C(51)-C(50)	113.6(5)
C(52)-C(51)-C(50)	109.0(5)
C(57)-C(55)-C(56)	107.6(5)
C(57)-C(55)-C(58)	106.9(5)
C(56)-C(55)-C(58)	109.5(5)
C(57)-C(55)-C(46)	111.0(4)
C(56)-C(55)-C(46)	114.0(4)
C(58)-C(55)-C(46)	107.5(5)
C(61)-C(60)-C(62)	108.4(6)
C(61)-C(60)-C(63)	107.3(5)
C(62)-C(60)-C(63)	105.3(5)
C(61)-C(60)-C(49)	114.6(5)
C(62)-C(60)-C(49)	109.5(5)
C(63)-C(60)-C(49)	111.3(5)
C(65)-C(64)-C(68)	108.4(4)
C(65)-C(64)-C(69)	125.1(4)
C(68)-C(64)-C(69)	126.5(4)
C(65)-C(64)-Ru(4)	69.3(2)
C(68)-C(64)-Ru(4)	71.6(3)

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

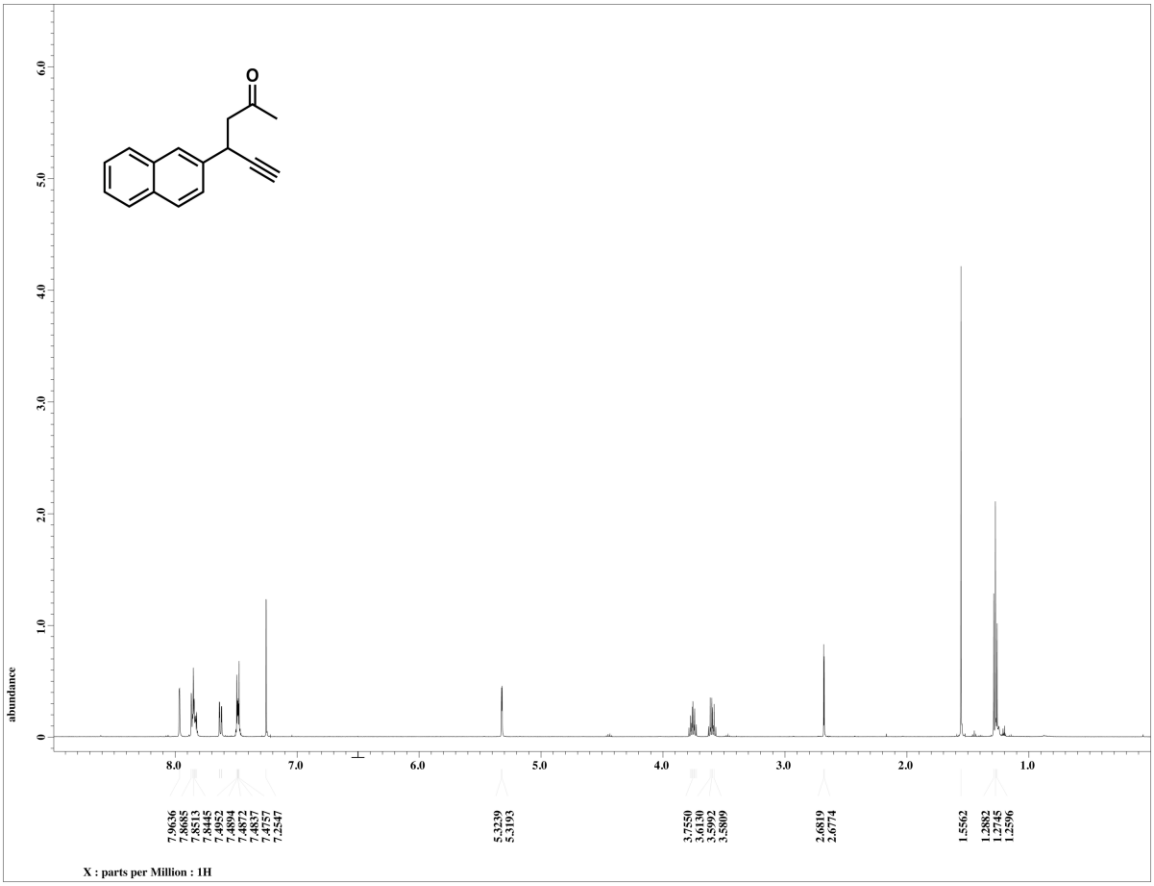
C(64)-C(65)-C(74)	133.7(4)
C(66)-C(65)-Ru(4)	70.5(3)
C(64)-C(65)-Ru(4)	73.0(3)
C(74)-C(65)-Ru(4)	128.7(3)
C(67)-C(66)-C(65)	107.2(4)
C(67)-C(66)-Ru(4)	74.9(3)
C(65)-C(66)-Ru(4)	71.6(3)
O(4)-C(67)-C(68)	122.9(4)
O(4)-C(67)-C(66)	125.2(4)
C(68)-C(67)-C(66)	111.9(4)
O(4)-C(67)-Ru(4)	128.2(3)
C(68)-C(67)-Ru(4)	71.8(3)
C(66)-C(67)-Ru(4)	68.2(3)
C(67)-C(68)-C(64)	104.3(4)
C(67)-C(68)-C(79)	122.4(4)
C(64)-C(68)-C(79)	132.4(4)
C(67)-C(68)-Ru(4)	72.0(3)
C(64)-C(68)-Ru(4)	70.1(2)
C(79)-C(68)-Ru(4)	129.8(3)
C(64)-C(69)-C(70)	119.6(4)
C(73)-C(70)-C(71)	110.4(5)
C(73)-C(70)-C(72)	108.2(5)
C(71)-C(70)-C(72)	106.1(4)
C(73)-C(70)-C(69)	113.8(4)
C(71)-C(70)-C(69)	106.9(4)
C(72)-C(70)-C(69)	111.2(4)
C(65)-C(74)-C(76)	110.6(4)
C(65)-C(74)-C(77)	107.6(4)
C(76)-C(74)-C(77)	106.1(4)
C(65)-C(74)-C(75)	114.1(4)
C(76)-C(74)-C(75)	106.4(4)
C(77)-C(74)-C(75)	111.8(5)
C(80)-C(79)-C(81)	108.9(4)
C(80)-C(79)-C(82)	105.6(5)
C(81)-C(79)-C(82)	107.4(4)
C(80)-C(79)-C(68)	115.1(4)

Table 3.5.6. Bond lengths [A] and angles [deg] for **70**.

Cl(4')-C(83')-Cl(3')	112.6
Cl(6)-C(84)-Cl(5)	112.6
Cl(6')-C(84')-Cl(5')	112.6
Cl(6")-C(84")-Cl(5")	112.6

3.6 NMR Data

For compound 71.



Chapter Four

Summary

4.1 Summary

Thiol-bridged diruthenium complexes are efficient catalysts for propargylic substitution reactions of propargylic alcohols with various heteroatom and carbon centered nucleophiles. However, these thiol-bridged diruthenium complexes are mostly limited to aromatic propargylic alcohols. Tertiary and aliphatic propargylic alcohols were rarely studied for propargylic substitution reactions. We explored new mono- and di-ruthenium complexes to overcome these limitations.

First, we explored trispyrazolyl borate derivatives as a ligand from which we can explore the electronic or steric environments on active ruthenium complexes. ^{cl}TpRu(COD)Cl was synthesized via a simple method and examined it for the propargylation reaction. It showed better catalytic reactivity than TpRu(COD)Cl for aromatic propargylic alcohols. Although this complex did not perform well with aliphatic or tertiary alcohols, ligand effects can have the potential to show different reactivity compared to common Cp or neutral ligands such as benzene derivatives.

Second, thiolate-bridged diruthenium complexes were synthesized and examined for catalytic activity in the propargylic substitution reaction. We introduced a more complicated Cp moiety to ruthenium, resulting in sterically more hindered diruthenium complexes. It was successfully synthesized, and the structure was confirmed by X-ray

crystallography. As we expected, the synthesis of di-or tri-thiolate bridged ruthenium complexes depended on the amount of $MeSSiMe_3$ as a thiol source.

The catalytic activity of ^{Cl}TpRu(COD)Cl for propargylic substitution reactions with aromatic propargylic alcohols was good, but the substrate scope was very limited. Unfortunately, the di-bridged ruthenium complex, [Cp^RuCl(μ-SMe)$_2$RuCp^Cl], afforded only trace amount of the desired product with aromatic propargylic alcohols. It seems that the bulky ligands may interfere with the substrates, approach to the allenylidine intermediate.